

Jiun-Haw Lee | David N. Liu | Shin-Tson Wu

Introduction to
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DISPLAYS**

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Introduction to Flat Panel Displays

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Introduction to Flat Panel Displays

Jiun-Haw Lee, David N. Liu and Shin-Tson Wu

Introduction to Flat Panel Displays

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Series Editor's Foreword

Article 2 of the bylaws of the Society for Information Display begins “*1. The purpose of SID shall be: a) To encourage the scientific, literary and educational advancement of information display and its allied arts and sciences. . .*”. This book series was begun eleven years ago with the express object of extending that encouragement, which in the printed form amounted to publishing conference proceedings and a Journal of peer refereed papers, to the provision of a series of books which would satisfy the needs of scientists and engineers working in the wide and complex field of displays. More recently in 2006, we published “Fundamentals of Liquid Crystal Devices” by Deng-Ke Yang and Shin-Tson Wu (who – not coincidentally – is a co-author of this book). That book extended the readership because it was written primarily as a post graduate textbook.

This latest volume in the series extends that educational scope still further by describing the operating principles and the methods of fabrication of technologies used or of potential use in flat panel displays, their methods of addressing, systems aspects and the underpinning science. Although general books on flat panel displays have been published in the past, this is the first comprehensive flat panel display textbook to have been written at this academic level. Its readership and its use will extend far beyond post graduate courses as it offers in a single volume material of great value to practising industrial engineers and scientists across the whole range of flat panel technologies.

In my foreword, I usually provide a précis of the contents of a book, but the authors have done this so comprehensively that such an effort on my part would be superfluous. It merely remains for me to thank them for the great effort they have put into writing this book and wholeheartedly to commend it to our present and expanding readership.

Anthony C Lowe
Series Editor
Braishfield, UK.

About the authors

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Jiun-Haw Lee received BSEE, MSEE and PhD degrees in electrical engineering in 1994, 1995 and 2000, respectively, all from National Taiwan University, Taipei, Taiwan. From 2000 to 2003 he was with the RiTdisplay Corporation as the director. In 2003 he joined the faculty of National Taiwan University in the Graduate Institute of Photonics and Optoelectronics and the Department of Electrical Engineering, where he is currently an associate professor. His research interests include organic light-emitting devices, display technologies and solid-state lighting.

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David N. Liu

David N. Liu has been the director of the Strategic Planning Division in the Display Technology Center (DTC) of the Industrial Technology Research Institute (ITRI) since 2006. He worked on IC and field emission displays at ERSO (Electronics Research and Service Organization)/ITRI and Bellcore (Bell Communication Research) from 1983 to 1996. He started his research and development work on plasma display panels at Acer Peripheral Inc. and AUO from 1996 to 2002. After his service at AUO, he was in charge of the flat panel display technology division in ERSO/ITRI until 2006.

Dr Liu received his PhD degree in electrical engineering from New Jersey Institute of Technology in 1992. He has over 45 issued patents, 18 published papers and a contributed chapter of the *Semiconductor Manufacturing Handbook* (McGraw-Hill, 2005). He also successfully developed field emission displays, plasma display panels and flat panel displays followed by the receipt of many awards from ITRI, Photonics Industry and Technology Development Association, Administration Bureau of Science Base Industry Park and the Ministry of Economic Affairs (MOEA). He was also a recipient of the Outstanding Project Leader Award from MOEA in 2006.

Shin-Tson Wu

Shin-Tson Wu is a PREP professor at the College of Optics and Photonics, University of Central Florida (UCF). Prior to joining UCF in 2001, Dr Wu worked at Hughes Research Laboratories (Malibu, California) for 18 years. He received his PhD in physics from the University of Southern California (Los Angeles) and BS in physics from National Taiwan University (Taipei).

Prof. Wu has co-authored four books: *Fundamentals of Liquid Crystal Devices* (Wiley, 2006), *Introduction to Microdisplays* (Wiley, 2006), *Reflective Liquid Crystal Displays* (Wiley, 2001) and *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, 1993), six book chapters, over 300 journal publications and 75 issued and pending patents.

Prof. Wu is a fellow of the IEEE, OSA, SID and SPIE. He is a recipient of the SPIE G.G. Stokes award, SID Jan Rajchman Prize, SID Special Recognition Award, SID Distinguished Paper Award, Hughes team achievement award, Hughes Research Laboratories outstanding paper award, UCF Distinguished Researcher Award and UCF Research Incentive Award. He was the founding editor-in-chief of the IEEE/OSA *Journal of Display Technology*.

3

Thin-film transistors

3.1 Introduction

Thin-film transistors (TFTs) are widely used as electronic switches to turn the pixels of active matrix liquid crystal displays (LCDs) and organic light-emitting devices (OLEDs) on and off.^{1,2} Typically, the silicon-based materials of TFTs are mainly in the amorphous or polycrystalline rather than the crystalline silicon phase. The reasons for using disordered silicon are: first, the diagonal size of a crystalline silicon wafer is limited to 12 inches, which makes fabrication of large-size displays using silicon wafers impossible; and second, the silicon substrate absorbs visible light, making it unsuitable as a substrate for transmissive LCDs. Also, it is technically difficult to epitaxially grow single-crystal silicon on glass substrates, since the melting point of glass is below 600 °C, far below that of silicon (1200 °C). In contrast, amorphous silicon, grown by low-temperature plasma-enhanced chemical vapor deposition (PECVD), can meet the basic requirements for driving LCDs, and it can provide a uniform thin film over a large area (ex: 2160 mm × 2460 mm). Polycrystalline silicon (poly-Si), made by excimer laser melting and recrystallization of an amorphous silicon thin film, has an increased grain size and hence a higher carrier mobility with the advantages of: (1) an increased aperture ratio due to the higher carrier mobility and (2) a suitability for use in system-on-panel fabrications due to higher performance transistors.³ But nonuniformity created during the recrystallization process and high leakage current resulting from the higher surface roughness are two major technological issues for poly-Si. Therefore, at present, most TFTs for LCD applications are based on amorphous silicon and related fabrication processes.

In this chapter, we first introduce some basic semiconductor concepts, which are essential background knowledge not only for TFTs but also for light-emitting diodes (LEDs; Chapter 6). Then, we discuss the material aspects of amorphous and poly-TFTs, followed by their electrical characteristics and the methods to drive a display. Finally, TFTs made from other materials such as organic materials and metal oxides are discussed.

3.2 Basic concepts of crystallized semiconductor materials

Before describing the characteristics of amorphous semiconductors with disordered structure, which are typically used in conventional TFTs, we introduce some basic properties of semiconductors with a single-crystal structure. A semiconductor is a solid-state material with a conductivity between that of an insulator (e.g. glass and quartz) and a conductor (e.g. silver, aluminum and gold).⁴ Typical semiconductor conductivities range from 10^{-8} to 10^3 S cm⁻¹. In an insulator, the conductivity is too low for carrier transport.

In a conductor, by contrast, carriers (electrons and holes) can propagate with little obstruction. The conductivity of a semiconductor can be tuned by means of electric fields and impurity concentrations, which makes it possible for them to be used in various electronic applications. For example, the conductivity of a TFT is modulated by an electric field and hence it can be used as an electronic switch. When doped with different atoms, a p- or n-type semiconductor can conduct by means of holes or electrons, respectively. When p- and n-type semiconductors are connected to each other, a p–n junction is formed that allows unidirectional carrier transport. This is the basic structure of the LED, as discussed in Chapter 6.

A semiconductor consisting of only one kind of atom, such as silicon and germanium which are located in group IV of the periodic table, is called an ‘elementary semiconductor’. In this chapter, we mainly focus on the widespread use of silicon in TFT switches due to the advantages of high performance, mature fabrication techniques and comparatively low cost. For LED applications, however, due to its indirect bandgap characteristics (Section 3.2.1), bulk single-crystal silicon cannot emit light efficiently. Hence, a compound semiconductor that combines two or more elements (e.g. gallium from group III and arsenic from group V, forming GaAs) is employed (as discussed in Chapter 6).

3.2.1 Band structure of crystallized semiconductors

A semiconductor with a single-crystal structure has long-range order, which means atoms in a crystallized semiconductor arranged with regular and repeated three-dimensional pattern. A group IV atom has four valence electrons (which will be described later) in its outer shell. The optimal number of covalent bonds it can form is $8 - 4 = 4$, which arises from the well-known ‘ $8 - N$ rule’. Hence, each atom in a silicon crystal is connected to four neighboring atoms equally distant from it but in different directions by covalent bonds, i.e. each atom shares four electrons with four neighboring atoms. Since the atoms are identical in an elementary semiconductor, it is straightforward to understand that the four connected neighboring atoms form an equilateral tetrahedron. Figure 3.1(a) shows the three-dimensional structure of single-crystal silicon. Each sphere represents a silicon atom that is connected to four other atoms by covalent bonds. For a compound semiconductor such as GaAs, the bonding configuration is similar to that of silicon, as shown in Figure 3.1(b). Larger black and smaller white spheres represent gallium and arsenic atoms, respectively. However, since different atoms attract valence electrons to different degrees, the bonding contains some ionic character, and is not purely covalent. The periodic structure of a crystallized semiconductor is usually called a lattice structure. Also, as shown in Figures 3.1, one can define a unit cell of the lattice, which is the smallest repeat unit required to generate the whole lattice. Also, the lattice constant represents the edge length of the unit cell, which is critical for epitaxial growth in LEDs, as discussed in Chapter 6.

Considering a single isolated atom, the nucleus at the center attracts electrons, which creates a Coulomb potential that is proportional to the inverse of the distance to the nucleus. There are many discrete energy states inside the potential well, as shown in Figure 3.2(a). To determine the electronic configuration in a semiconductor, the Pauli exclusion principle is applied, which states that each electron must exhibit an identical quantum state. For an energy state in Figure 3.2(a), two electrons can fill one energy state since they exhibit different spin angular momentum vectors (orientation specified by spin-up and spin-down). Lower energy states are filled first with the inner shell electrons. Outermost electrons, partially or completely filling the high energy state, are called valence electrons, as mentioned above. When two atoms approach closely and form a bond, each energy level splits into two discrete states, as shown in Figure 3.2(b). Electrons from the two atoms are reallocated again from low to high energy states in this new system. Again, in a crystal, there are lots of atoms, typically with a concentration of 10^{23} cm^{-3} . Hence, each energy level in an isolated atom splits into very many closely packed states, which is called an energy band, as shown in Figure 3.2(c).^{5, 6} Also in this system, inner electrons fill the bands sequentially from the lowest to the highest energy state. Finally, valence electrons completely fill an energy band,

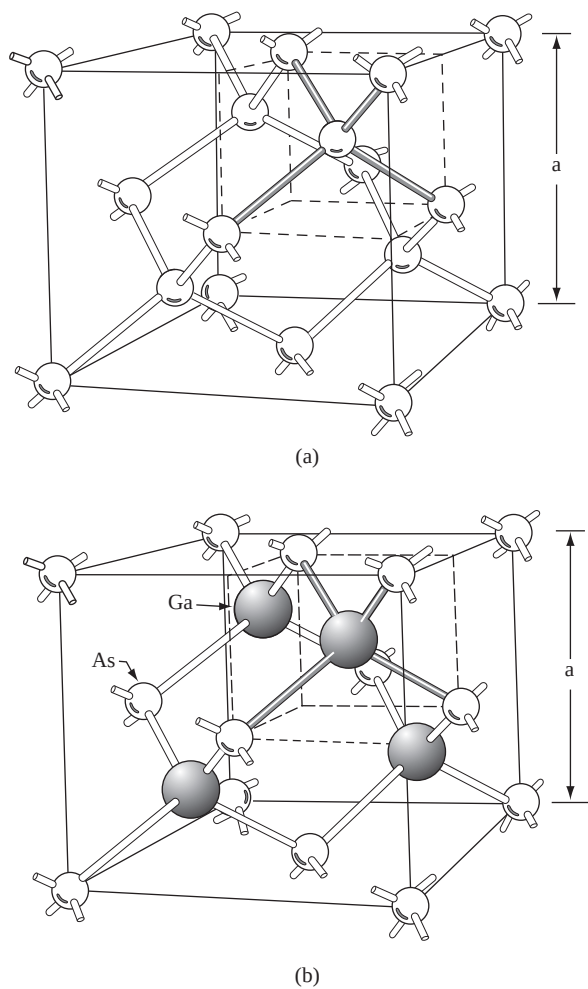


Figure 3.1 Three-dimensional crystalline structure of (a) silicon and (b) GaAs.⁴

namely the valence band that represents the highest energy state occupied by electrons. This happens at 0 K without thermal effects.

Sometimes a valence electron is also called a bonding electron, since it is shared by neighboring atoms. Because the valence electrons are the outmost electrons of an atom, they experience a much smaller influence from the nuclei due to the shielding effect of the inner shell electrons. When considering the temperature effect ($T > 0$), these valence electrons can obtain thermal energy and escape from the covalent bond, and can then be treated as ‘free electrons’ with the introduction of effective mass concept, which will be described later in this chapter. In the energy band diagram described above, this means the valence electron jumps to the next higher energy state, which is called the conduction band, as shown in Figure 3.3. The energies of the top of the valence band and the bottom of the conduction band are denoted E_v and E_c , respectively. The energy difference between the conduction and valence bands is called the bandgap (E_g); no energy level is allowed between these two bands. The higher the temperature the more electrons are promoted to the conduction band. At the same time, this leaves ‘holes’ with positive charge in the

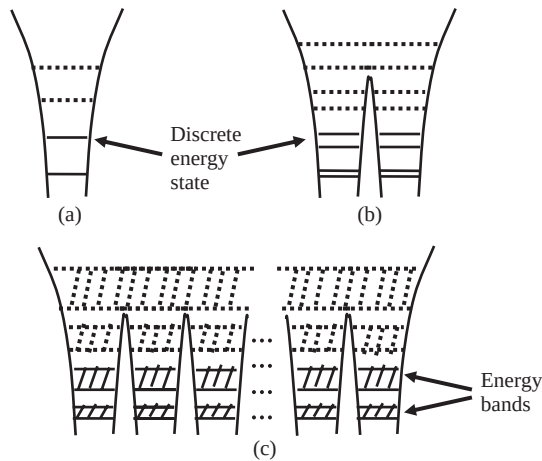


Figure 3.2 Energy levels in (a) an isolated atom, (b) two atoms and (c) a crystal structure. Solid and dashed lines depict the occupied and unoccupied energy states (bands).

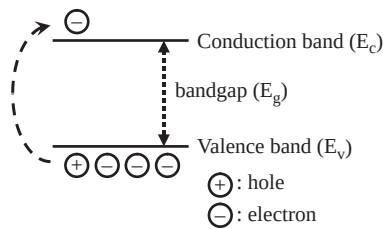


Figure 3.3 Energy band structure.

lattice. An electron from another covalent bond neutralizing a hole creates another hole, and so on. Hence it appears that holes are transported in a crystal, in a direction opposite to that of the electron movement.

At 0 K, all the electrons are in the valence band. As the temperature increases, some electrons obtain enough thermal energy to move up to the conduction band. In a semiconductor, the statistical distribution of electrons at different energies is typically described by the concept of Fermi energy (or Fermi level). Under thermal equilibrium at a certain temperature, the probability (F) of finding an electron at energy level E is expressed as

$$F(E) = \frac{1}{1 + \exp[(E - E_F)/(kT/q)]}, \tag{3.1}$$

where E_F is the Fermi level (in eV) and k and T are the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$) and absolute temperature (in K), respectively. Equation (3.1) is derived from quantum mechanics and is called the Fermi–Dirac distribution. This can be applied to the statistical distribution of any particle obeying the Pauli exclusion principle. From the above equation, it is evident that when $E = E_F$, $F(E) = 0.5$, which means this energy level is occupied by an electron with 50% probability. Figure 3.4 shows plots of $F(E)$ curves versus energy at different temperatures. When T is close to 0 K, $F(E)$ is a step function, i.e. $F(E)$ is 1 and 0 when E is lower and higher than E_F , respectively. On increasing the temperature, the $F(E)$ curves tend to decrease and increase below and above E_F , which means the probability of an electron occupying a higher energy increases. In other words, the electron concentration in the conduction band increases with increasing temperature.

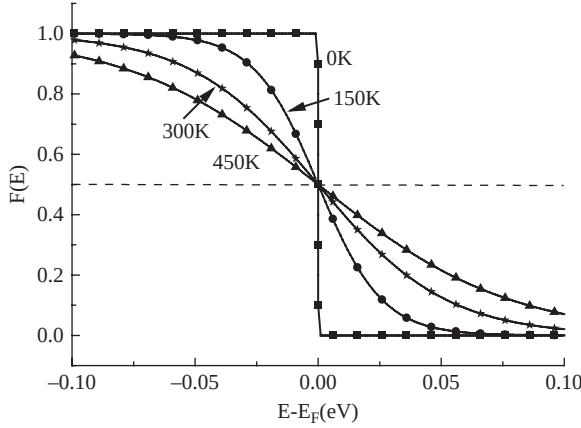


Figure 3.4 $F(E)$ curves at different temperatures.

Because of the wave properties of particles, an object exhibits a de Broglie wavelength (λ) given by

$$\lambda = \frac{h}{p} \quad (3.2)$$

or

$$\lambda = \frac{2\pi}{k}, \quad (3.3)$$

where $h = 6.626 \times 10^{-34}$ J s is the Planck constant and p and k are the momentum and wavenumber of the 'particle wave', respectively. The kinetic energy (E) of this object can be represented as

$$E = \frac{p^2}{2m} \quad (3.4)$$

or

$$E = \frac{(h k / 2\pi)^2}{2m} \quad (3.5)$$

or

$$\frac{d^2 E}{dk^2} = \frac{(h/2\pi)^2}{m}, \quad (3.6)$$

where m is the mass of the object. According to Equation (3.2), the de Broglie wavelength is inversely proportional to momentum. For example, a baseball with a mass of 0.145 kg has a de Broglie wavelength of 1.03×10^{-34} m when moving at 160 km h⁻¹. This wavelength is too small to be measured. Hence, it is difficult to observe the wave characteristics of objects in daily life since they are too heavy. By contrast, the mass of an electron in free space (m_0) is very small, i.e. 9.1×10^{-31} kg. When an electron moves in a semiconductor, due to the interaction with the atoms, its effective mass (discussed later) is even smaller, i.e. $0.19m_0$ in silicon for a certain transport direction. For a typical velocity of 10^7 m s⁻¹, its de Broglie wavelength is about 3.84×10^{-10} m (or 3.84 Å). This value is comparable to the lattice constant of crystal-line structures (5.43 and 5.65 Å for silicon and GaAs, respectively), which means the electron wave will experience diffraction by the lattice. Hence, the E - k relationship is no longer a parabolic form as shown in Equation (3.4). The detailed E - k band structure can be calculated from quantum mechanical theory.

Figure 3.5 shows the E - k band structures of silicon and GaAs, where $E = 0$ corresponds to the maximum of the valance band. One can see that there are bandgaps between the maximum of the valance

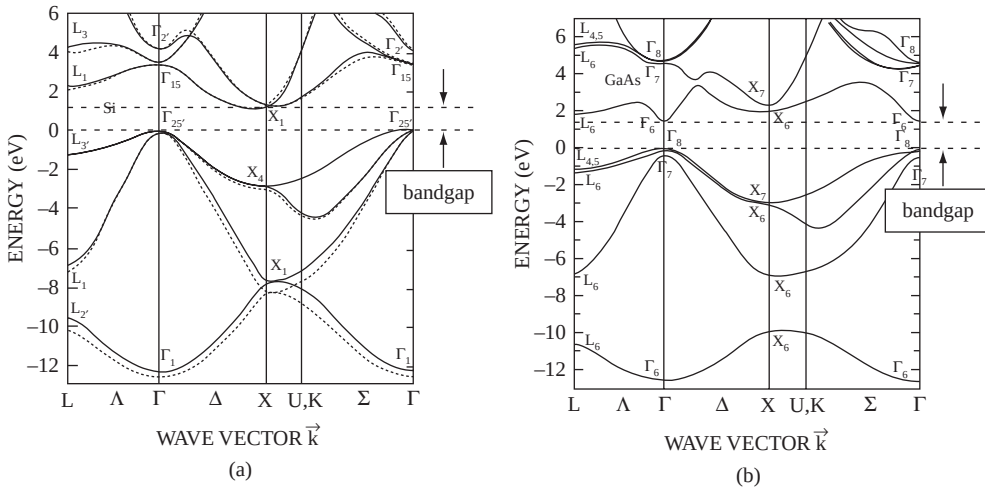


Figure 3.5 Calculated E - $\mathbf{k}$ band structures of (a) silicon and (b) GaAs.⁷ The solid and dashed lines in the silicon band structure show results obtained from two different kinds of calculations. Source: J.R. Chelikowsky, and M.L. Cohen, *Nonlocal pseudopotential calculations for the electronic structure of eleven diamond and zinc-blende semi-conductors*, Phys. Rev. B, 14, 556 (1976). Reprinted with permission from the American Physical Society.

band and the minimum of the conduction band. Excited electrons accumulate near the minimum of the conduction band since this is energetically favorable. The corresponding holes are located near the maximum of the valence band for the same reason. The vertical axis shows different $\mathbf{k}$ vectors which can be regarded as viewing the lattice from different angles. Since the atoms are arranged in the ordering shown in Figure 3.1, electrons moving in different directions experience different periods and diffraction effects from the nuclei. For silicon, the two extremes have different $\mathbf{k}$ vectors, where the top of the valence band and the bottom of the conduction band are at the Γ and X points on the $\mathbf{k}$ -axis, respectively; the material is called an indirect bandgap semiconductor. In contrast, for GaAs, the two extremes coincide at the Γ point and it is called a direct bandgap semiconductor. The difference in band structure between direct and indirect bandgap semiconductors results in different optical characteristics, discussed further in Chapter 6. We note that near the minimum of the conduction band and the maximum of the valence band, the E - $\mathbf{k}$ curve has a nearly parabolic shape, where most carriers accumulate. Hence, one can slightly modify Equations (3.5) and (3.6) to describe the motion of an electron in the conduction band of a semiconductor:

$$E = \frac{(\hbar\mathbf{k}/2\pi)^2}{2m^*} \quad (3.7)$$

and

$$\frac{d^2E}{d\mathbf{k}^2} = \frac{(\hbar/2\pi)^2}{m^*}, \quad (3.8)$$

where m^* is called the effective mass, which can be obtained provided that the E - $\mathbf{k}$ relationship is known.

3.2.2 Intrinsic and extrinsic semiconductors

A semiconductor without other impurity atoms is called an intrinsic semiconductor. In such a material, electrons and holes in the conduction and valence bands (free electrons and holes) are generated simultaneously, typically from thermal energy. Hence, the concentrations of the free electrons and holes can be described as

$$n = p = n_i, \quad (3.9)$$

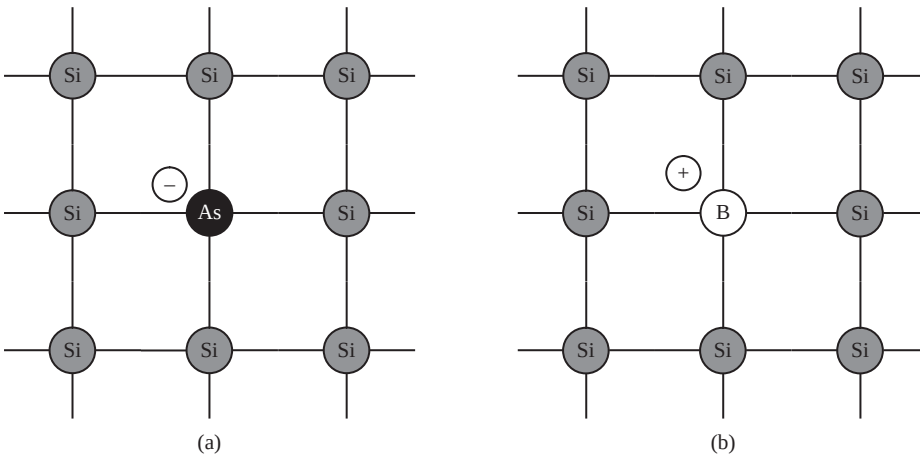


Figure 3.6 Schematic of bonding of silicon with (a) arsenic and (b) boron impurities.

where n and p are electron and hole concentrations, respectively, and n_i is the intrinsic carrier density, which is dependent on the temperature and bandgap energy. Obviously, for a higher temperature or a smaller bandgap, it is easier to generate more electron–hole pairs, corresponding to a larger n_i value.

One might intentionally add some impurities into a semiconductor to vary the conductivity. This is called an extrinsic semiconductor. As shown in Figure 3.6, incorporating group V atoms such as arsenic and group III atoms such as boron into silicon generates one more electron and one more hole, respectively, which effectively increases the carrier concentrations. This is called n- and p-type doping since the conducting carriers are electrons and holes, respectively. Here, group V and III dopants are typically called donors and acceptors, since they respectively ‘donate to’ and ‘accept from’ the silicon atom an electron.

Typically, in a crystalline semiconductor, these extra electrons or holes can be treated as nearly free, which is called the complete ionization condition. This is not the case for some III–V semiconductors, especially for the wide bandgap materials described in Chapter 6. For an n-type semiconductor, since there are free electrons released from the donors, the electron concentration is higher than that of holes. This means it is easier to find a free electron in the conduction band than in the intrinsic semiconductor case, and the E_F level shifts toward the conduction band level E_c . In contrast, for a p-type semiconductor, E_F moves down toward the valence band level E_v . For an intrinsic semiconductor, E_F is typically very close to the center between E_c and E_v . Hence, one can determine whether a semiconductor is of n- or p-type by observing whether E_F lies at the upper or lower half of the bandgap, respectively. Theoretically, electron concentration (n) can be obtained from

$$n = \int N(E)F(E) dE, \quad (3.10)$$

where $N(E)$ is the density of states, which indicates how many carriers this energy state allows. In the bulk of a crystalline material, $N(E)$ is proportional to $E^{0.5}$, and the value is zero for $E < E_c$. This means there is no allowable state within the bandgap. Increasing the energy above E_c leads to more and more allowable states. In contrast, the probability of finding an electron decreases exponentially as the energy increases, as shown by Equation (3.1). Although Equation (3.10) has no analytical solution, we can still

obtain the following equations under the approximation of a low carrier concentration condition, i.e. $<10^{18} \text{ cm}^{-3}$:

$$p = n_i \exp\left(\frac{E_i - E_F}{kT/q}\right), \quad (3.11)$$

$$n = n_i \exp\left(\frac{E_F - E_i}{kT/q}\right), \quad (3.12)$$

$$pn = n_i^2, \quad (3.13)$$

where E_i is the center of the bandgap (in eV). Note that these three equations are valid for both intrinsic and extrinsic conditions. When the Fermi level is shifted from E_i toward the valence band, the hole concentration increases; when E_F moves up from E_i toward E_c , the electron concentration increases. The product of Equations (3.11) and (3.12) yields Equation (3.13), which shows that the product of electron and hole concentrations is a constant that is the same for intrinsic and extrinsic semiconductors. This means that, for example, it is possible to dope donors to increase electron concentrations. However, at the same time, hole concentrations decrease, and vice versa. For an extrinsic semiconductor, under complete ionization condition, one can also write

$$p = N_A, \quad (3.14)$$

$$n = N_D, \quad (3.15)$$

where N_A and N_D are acceptor and donor concentrations, respectively.

Example 3.1

Find the carrier concentrations in silicon doped with boron at a concentration of $10^{16} \text{ atoms cm}^{-3}$ at 300 K. Also find the energy difference (in terms of eV) between the Fermi level and the top of the valence band ($n_i = 1.45 \times 10^{10} \text{ cm}^{-3}$ and $E_g = 1.12 \text{ eV}$ at this temperature).

Answer. Assuming complete ionization, from Equations (3.4) and (3.13),

$$p = N_A = 10^{16} \text{ cm}^{-3},$$

$$n = \frac{n_i^2}{p} = \frac{(1.45 \times 10^{10})^2}{10^{16}} = 2.1 \times 10^4 \text{ cm}^{-3}.$$

From Equation (3.11),

$$E_i - E_F = \frac{kT}{q} \ln\left(\frac{p}{n_i}\right) = \frac{1.38 \times 10^{-23} \times 300}{1.6 \times 10^{-19}} \ln\left(\frac{10^{16}}{1.45 \times 10^{10}}\right) = 0.35 \text{ eV}$$

$$E_F - E_v = \frac{1.12}{2} - 0.35 = 0.21 \text{ eV}.$$

3.3 Disordered semiconductors

Amorphous silicon (a-Si) consists of silicon atoms without a crystallized structure (no long-range order). However, a-Si retains short-range order, which means that a silicon atom forms covalent bonds with four neighboring atoms but with variations in bonding length and angle.⁸ Due to the nonperiodic structure, it is not possible to draw E - $\mathbf{k}$ band diagrams. Instead, the concept of density of states is used to describe the

electrical and optical characteristics of a-Si. Since atoms in the a-Si network exhibit statistical differences in bonding conditions, there are some allowed states extending from the conduction and valence bands, which are called tail states. Due to the imperfect crystalline structure, there are also lots of dangling bonds, which can be viewed as defects, from the viewpoint of crystalline silicon. Those defects can be described as the deep state with energy inside the bandgap. Carriers with lower energy will be trapped or localized by these states which become immobile. When the number of injected carriers is large enough, high energy carriers can hop within the random network, giving a finite mobility value much lower than that in crystalline silicon. Typically, we can classify silicon in terms of crystallization (grain size), as shown in Figure 3.7.⁹ In a-Si material, which is viewed as the most disordered system, the mobility is as low as 1 and 0.01 cm² V⁻¹ s⁻¹ for electrons and holes, respectively. When silicon atoms form a crystalline structure of the order of several to several tens of nanometers, the silicon is called nanocrystalline silicon (nc-Si), with higher mobility values. On increasing the grain size to the micrometer range, the classifications are called microcrystalline silicon (μc-Si) and polycrystalline silicon (poly-Si). The increase of grain size from a-Si to nc-Si and even μc-Si can be achieved by optimization of fabrication parameters during thin-film deposition. However, to obtain poly-Si, melting and recrystallization processes are typically needed, which require a temperature (1200 °C) that is much higher than the softening temperature of glass substrates, i.e. 600 °C. But local heating by laser irradiation makes it possible to form high-quality poly-Si thin film on glass or even plastic substrates. In this section, we describe the material characteristics, preparation and carrier transport of a-Si and poly-Si, which are the two most commonly used materials in display technologies.

3.3.1 Amorphous silicon

Figure 3.8 shows schematically the structure and density of states of a-Si. One can see that a-Si has a random structure without long-range order.¹⁰ Hence, it is not possible to obtain the *E-k* band diagram as in Figure 3.5. However, one can describe the carrier concentrations at different energies with the concept of density of states, i.e. how many states are allowed at a certain energy level, and then determine the electrical bandgap and optical bandgap of a-Si. The larger and smaller spheres in Figure 3.8(a) represent silicon and hydrogen atoms, respectively. Hydrogen atoms are introduced during thin-film formation by

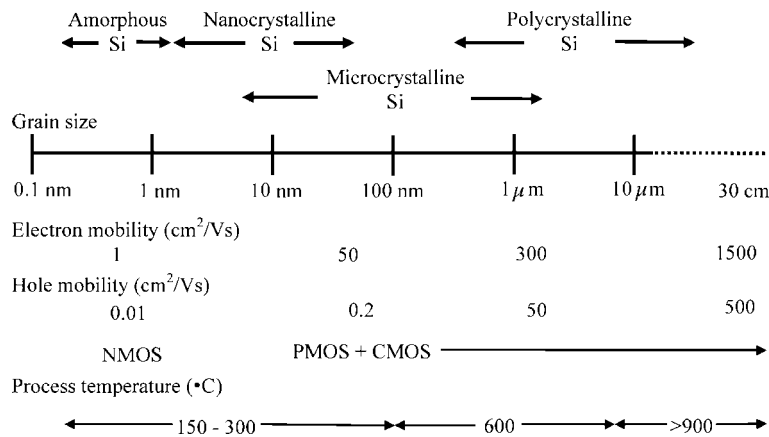


Figure 3.7 Classification of silicon by grain size, together with the mobility values and process conditions.⁹ (Reprinted from Wagner, S., Gleskova, H., Cheng, I.C. and Wu, M. (2003) Silicon for thin-film transistors. *Thin Solid Films* 430, 15. Copyright (2003), with permission from Elsevier)

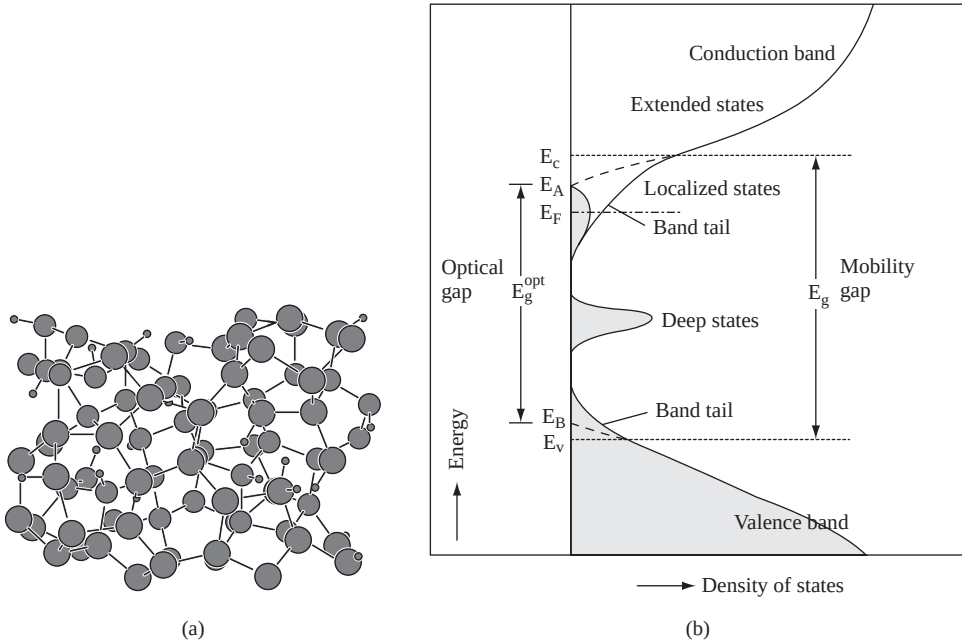


Figure 3.8 (a) Three-dimensional structure of a-Si:H.⁸ (Street, R.A. (ed.) (1999) *Technology and Applications of Amorphous Silicon*. With kind permission of Springer Science and Business Media.) (b) Density of states of a-Si:H.¹⁰ (Source: Tsukada, T. (2003) *TFT/LCD: Liquid-Crystal Displays Addressed by Thin-Film Transistors*. Permission of Taylor & Francis.)

PECVD, which will be described later. Hydrogen atoms effectively reduce the number of dangling bonds in a-Si with Si–H bonding. Typically, a-Si is written as a-Si:H, which means the a-Si is hydrogenated. Although hydrogen atoms can passivate a large number of dangling bonds in the a-Si:H network, there are still lots of bonding defects, which are the origins of the deep states in Figure 3.8(b) within the bandgap.

As shown in Figure 3.8(a), a-Si can be viewed as a random network connected by covalent bonds without long-range order. Although each silicon atom is still fourfold coordinated, the bonding length and angle are different, which results in the extension of the density of states inside the forbidden gap. These are the tail states in Figure 3.8(b). In crystalline silicon, electrons are transported within the ordered network; this is similar to the free electron case and can be described by the effective mass concept. However, in a-Si material, electrons are confined within a grain, which is called the localized state, and can hop to other grains when they obtain enough kinetic energy, which is called the extended state. When electrical current is injected into a-Si, the excess carriers fill the deep levels first, and then the localized states. At this time, those carriers contribute little to electrical conduction. With a further increase in the injected current, carriers fill the extended states, which leads to a much lower mobility value compared to that of crystallized silicon. Due to the carrier trapping and escaping process, the operating speed of a-Si-based devices is limited. The low mobility value results in high resistivity according to

$$\rho = \frac{1}{nq\mu}, \quad (3.16)$$

where ρ is the resistivity (in Ω cm), q is the carrier charge and μ is the carrier mobility. Typically, for undoped or n-type a-Si, conduction from holes can be ignored since the hole mobility is much lower than the electron mobility. One can define the mobility gap (electrical bandgap) from the difference in

the localized state energies, which is about 1.9 eV. This bandgap is larger than the bandgap of crystalline silicon (1.1 eV). The high 'bandgap' value can be understood from the fact that a-Si exhibits nonzero mobility when the localized states are filled up, rather than the onset of the tail states. As mentioned above, it is not possible to obtain the $E-k$ band diagram for a-Si due to its random structure. Hence, the selection rule for direct and indirect transitions is relaxed in this material. It also results in a-Si having a higher absorption coefficient for photons, compared to crystalline silicon with indirect bandgap characteristics. Consequently, one of the important applications for a-Si is in photovoltaic devices. Due to the complex structure of a-Si, there is no clear cutoff for the absorption edge. Typically, one can define an optical bandgap with a value of about 1.7 eV, which represents the onset energy of optical absorption.

As regards a-Si fabrication, PECVD is a common technique for producing a-Si:H thin film, at low temperature, of high quality and large area.⁹ Figure 3.9 shows schematically a PECVD system. Here, SiH_4 is used as the source for silicon deposition. Hydrogen gas is added to further passivate the dangling bonds of the silicon. Plasma generated by radiofrequency (rf) power decomposes the SiH_4 into Si and H radical ions, which then deposit on the substrate. The standard substrate temperature is about 250 °C which allows the radical atoms to migrate and form chemical bonds. To obtain high-quality a-Si:H with high throughput at a certain temperature limited by a glass (<600 °C) or flexible (<200 °C) substrate, fabrication parameters such as flow rate, rf power, chamber pressure, substrate temperature, SiH_4/H_2 ratio and gas source (NH_3 , SiCl_2H_2 , Si_2H_6 , etc.) should be taken into consideration and optimized. Also, under some process conditions, such as smaller SiH_4/H_2 ratio, higher plasma power density and thicker thin film, one tends to obtain nc-Si or even $\mu\text{c-Si}$, rather than a-Si.

3.3.2 Polycrystalline silicon

There are many advantages in the use of poly-Si rather than a-Si, since it exhibits a larger grain size and hence has better electrical properties, as shown in Figure 3.7. As mentioned above, a TFT is opaque and sensitive to visible light, so shielding is needed to block illumination of the device, which means the TFT area does not contribute to the information of the display. Better TFT electrical properties can give rise to the possibility of reducing the TFT dimensions, which can further: (1) enhance the display area for each pixel (called the aperture ratio), giving a higher luminance output, and (2) increase the display resolution. Also, due to the increase in the hole mobility, it is possible to fabricate not only n-type but also p-type TFTs. The performance (especially mobility and speed) of p- and n-type poly-Si TFTs is good enough for them also to be used in the peripheral circuits on glass substrates (rather than only for the switch element in pixels of a-Si TFT-based displays), which could greatly reduce the cost of the driving integrated circuits (ICs) and the complexity of manufacture.

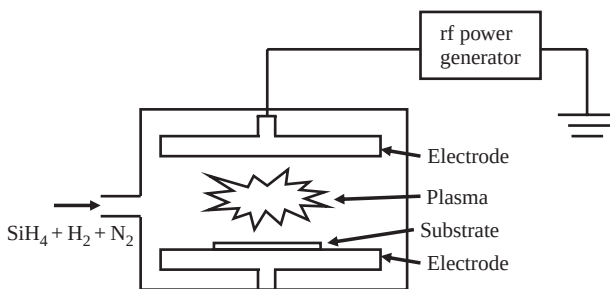


Figure 3.9 Schematic of a PECVD system.

A feasible way to obtain high-quality poly-Si is to melt a-Si with no (or little) heating of the substrate. During the process of cooling silicon from the liquid to the solid state, the silicon recrystallizes from some silicon seeds, and forms grains of larger size. Typically, a laser with radiation of a suitable wavelength, which can be effectively absorbed by the a-Si but to which the glass substrate is transparent, is selected for melting the a-Si and transforming it into poly-Si.¹¹ As mentioned above, a-Si contains many hydrogen atoms formed during thin-film growth by PECVD. Under high-power laser irradiation, the Si-H bonds break quickly to form a large amount of H₂ gas that escapes out of the poly-Si, leading to film ablation. Hence, a dehydrogenation process is needed before recrystallization; this is achieved by heating the substrate or irradiating with a laser beam of lower power density. However, after forming grains of larger size, there are still many traps at the grain boundaries; another hydrogenation process is required to passivate these dangling bonds. Typically, the defect density decreases by one order of magnitude after this passivation process, compared to the as-grown poly-Si.

As regards choosing a suitable laser to melt silicon, a shorter wavelength is preferred since the associated absorption coefficient is larger. However, if the laser wavelength is too short the laser radiation will be absorbed by the glass substrate. Typically, a XeCl excimer laser with an emission wavelength of 308 nm is used for silicon recrystallization; the process is called excimer laser crystallization. Although xenon is an inert gas, it reacts with chlorine and forms Xe⁺Cl⁻ when promoted from the ground to the excited state. It then releases the energy to return to the ground state, emitting light in the process, and finally splits into Xe and Cl atoms. The XeCl laser is a pulsed laser with a pulse duration of several tens of nanoseconds. During this short period, the silicon film will be heated up above the melting point. It then cools and forms larger grain boundaries. Also, because of the short pulse width, there is not too much heat generated, and it can dissipate with little or no heating of the substrate. Glass has a low thermal conductivity and the heat may melt only the surface of the glass substrate. However, the heat can quickly dissipate to the air from the other side of the glass.

The laser crystallization process converts optical energy into the thermal energy used to melt silicon. Since the light propagates from the surface of the silicon thin film toward the glass substrate, the silicon at the top melts first. When the laser fluence increases, more silicon becomes liquid and finally the whole thin film is completely melted. Figure 3.10 shows the mobility and grain size as functions of laser fluence. There is a clear linear dependence between these two parameters. Microscope images of poly-Si thin films are also shown. One can see that the grain size and TFT mobility increase at first and then decrease as the laser fluence increases. Under exposure to the low energy laser beam, the film is uniform and of a-Si phase without being transformed into poly-Si; the grain size and TFT mobility are kept low. When the pulse energy increases, a-Si starts to melt and poly-Si is formed at the top surface of the thin film.

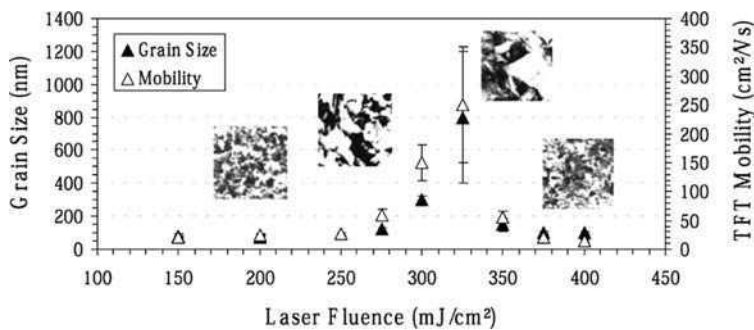


Figure 3.10 Grain size, TFT mobility and photographs of thin films under laser irradiation of different fluences.¹² (Reprinted from Voutsas, A.T. (2003) A new era of crystallization: advances in polysilicon crystallization and crystal engineering. *Appl. Surf. Sci.*, **208–209**, 250. Copyright (2003), with permission from Elsevier.)

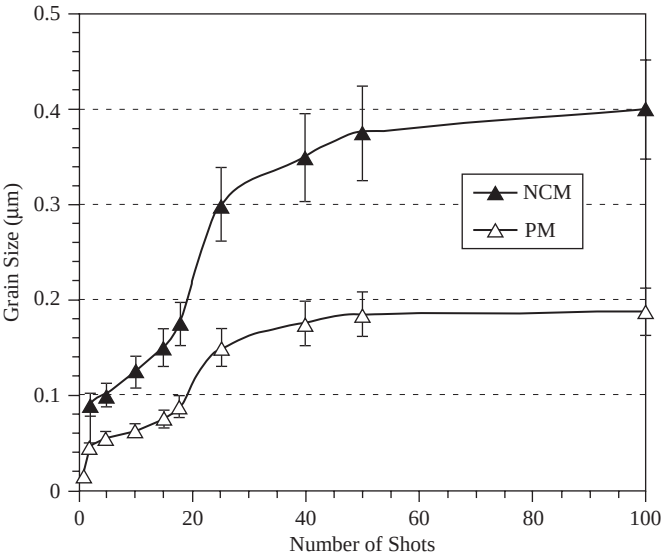


Figure 3.11 Grain size as a function of number of shots (NCM, near complete melting; PM, partial melting).¹² (Reprinted from Voutsas, A.T. (2003) A new era of crystallization: advances in polysilicon crystallization and crystal engineering. *Appl. Surf. Sci.*, **208–209**, 250. Copyright (2003), with permission from Elsevier.)

At this stage, the melt depth is less than the film thickness, and poly-Si solidifies vertically from the seeds provided by the underlying a-Si, which is called the partial-melting region. As the laser fluence further increases, the thin film is melted through. However, there is still some silicon remaining in the solid phase at the thin film–glass interface. This silicon forms discrete islands, rather than a continuous film, which provide seeds for the recrystallization process. When the pulse energy is further increased, the number of nucleation sites decreases, meaning that the grain size increases. The growth is not only vertical in direction but also lateral. During this stage, the grain size and TFT mobility increase with increasing laser fluence, and they reach a maximum at about 325 mJ cm^{-2} , as shown in Figure 3.10. This is called the near-complete-melting region. When the laser energy is very high, the whole thin film and the nucleation sites are molten. Nucleation starts somewhere in the liquid silicon, and hence the crystallization is nearly homogeneous without preferred directions, and the grain sizes decreases again. This is called the complete-melting region.

One can see that, although it is possible to obtain poly-Si with a large grain size and high mobility, the process window is quite small ($<50 \text{ mJ cm}^{-2}$), which results in difficulty in manufacturing stable TFTs of large size. Since the irradiation area of the excimer laser beam is typically much smaller than the glass substrate, a scanning stage is used for the process which requires a uniform and stable laser beam. To expand the experimental tolerance and further improve device performance, one can use the multishot line beam scanning technique. As shown in Figure 3.11, with increasing numbers of shots, the grain size significantly increases and the shot-to-shot variation decreases.

3.4 Thin-film transistor characteristics

A TFT is a device with three terminals. One is called the gate (G), which acts as a switch to open or close the other two terminals, called the source (S) and drain (D), as shown in Figure 3.12. In an a-Si TFT, the conducting carriers are electrons. Electrons drift from the source electrode to the drain, which results in

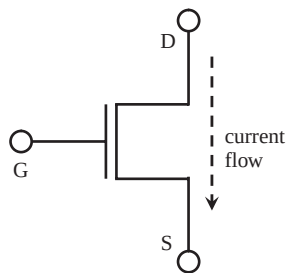


Figure 3.12 Schematic representation of and notation for a TFT.

current flow from drain to source. The switching structure is based on the metal–insulator–semiconductor (MIS) structure, which is also used widely in the IC industry with crystalline silicon. In such a structure, the metal can attract and repel carriers at the semiconductor side, which changes the carrier concentration of the semiconductor. It effectively engineers the conductance and hence can be used to switch on and off with high and low conductance, respectively. Although operation modes for crystalline silicon, a-Si and poly-Si are different, the basic physics is similar. Here, we focus on the electrical characteristics of a-Si and poly-Si.

Figure 3.13(a) shows the energy band diagram of an ideal MIS structure when $V_G = 0$. Here, we first consider the semiconductor as crystalline silicon with a perfect lattice and no traps. Figure 3.13 implies that the work function of the metal (ϕ_m , which is the energy needed to promote an electron from the metal to a vacuum) is aligned with the Fermi level of the semiconductor, which is not always true with different metal and semiconductor materials. The insulator has a very large bandgap and there is no carrier inside this layer. When applying a positive voltage on the metal side, negative charges are attracted at the surface of the semiconductor, as shown in Figure 3.13(b). Those carriers pile up at the semiconductor–oxide interface which effectively increases the electron density at this boundary. From Equation (3.12), we can see that the increase in electron density means the Fermi level and E_c become closer, which results in the band bending of the conduction and valence bands, as shown in Figure 3.13(b). In a uniform semiconductor layer (same material and doping concentrations), the Fermi level must be kept flat. If not, electrons will flow from the high to low E_F position until it becomes flat since the Fermi energy describes the probability of an electron occupying an energy state. In Figure 3.13(a) all the bands are flat; this is usually called the flat band condition, which is not necessary the case at $V_G = 0$ for nonideal cases.

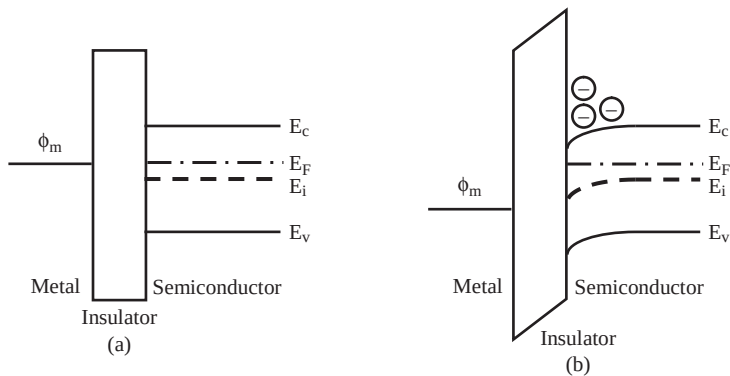


Figure 3.13 Band diagram of an ideal MIS structure at (a) $V_G = 0$ and (b) $V_G > 0$.

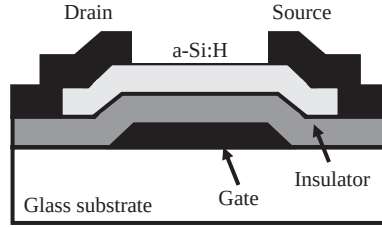


Figure 3.14 Cross-section of an a-Si TFT.

When using a-Si as the semiconductor material, the band bending behavior is similar to that of crystalline silicon, as shown in Figure 3.13, with some small modifications. The flat band condition at $V_G = 0$ is typically true for an a-Si TFT.¹³ However, when applying a positive voltage to the metal electrode (small V_G), due to the trap states in a-Si, electrons accumulate at the oxide–semiconductor interface, first filling deep states and tail states with zero mobility. At this time, these carriers are localized and immobile. On further increasing the voltage to V_G , say over a threshold voltage (V_T), a thin layer forms with mobile carriers at the oxide–semiconductor interface. Hence, one can use V_G to create and control an electron path at this interface, which is called the channel.

Figure 3.14 shows a cross-section of an a-Si TFT fabricated on a glass substrate. The gate electrode is deposited first, which is typically chromium, tantalum or aluminum. An insulating layer is then formed uniformly (using PECVD) covering the gate electrode, which can be silicon nitride (SiN_x) or silicon oxide (SiO_x). Then, a-Si is deposited on the top of the insulator as an MIS structure. On the right and left of the a-Si layer, source and drain electrodes are then formed, which typically consist of multiple layers, i.e. heavily doped n-type a-Si (n^+ a-Si) followed by chromium/aluminum, and n^+ a-Si forms an ohmic contact with the channel layer (a-Si) for better electron injection. The gate voltage affects the channel conductance and controls the on/off switching of this conductance. Current through drain to source (I_D) is modulated by the gate, which is also dependent on the drain voltage (V_D). Typically, the source is grounded ($V_s = 0$). The I – V characteristics of an a-Si TFT can be described by the following equations, which are similar to those for crystalline silicon devices:

$$I_D = \frac{1}{2}(\mu_n C_i) \left(\frac{W}{L} \right) [2(V_G - V_T)V_D - V_D^2], \quad 0 \leq V_D \leq V_G - V_T, \quad (3.17)$$

$$I_D = \frac{1}{2}(\mu_n C_i) \left(\frac{W}{L} \right) (V_G - V_T)^2, \quad V_D > V_G - V_T, \quad (3.18)$$

where μ_n is the electron mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$), C_i is the capacitance per unit area of the insulator layer (F cm^{-2}), W is the channel width, L is the channel length (distance between the source and drain) and V_T is the threshold voltage.

Figure 3.15 shows typical electrical characteristics of an a-Si TFT with channel width and length of 200 and 27 μm , respectively. Figure 3.15(a) shows the I_D – V_D curves for different V_G values, which are typically called output characteristic curves. For a positive and sufficiently large V_G , there are mobile electrons which make the channel conductive. Then, with increasing V_D , I_D continues increasing until $V_D = V_G - V_T$, which is called the linear region. Since the channel region is somewhat like a resistance, it is reasonable that higher V_D results in higher current. On further increasing the voltage, the channel cannot support a higher current density, leading to a saturation region. The saturation current increases with increasing gate voltage since it attracts more electrons accumulating at the insulator–semiconductor interface. Figure 3.15(b) shows the $\log(I_D)$ – V_G curves at $V_D = 0.1$ and 10 V, which are also called the transfer characteristic curves. When $V_D = 10$ V, one can see that, with increasing V_G , I_D is very low (about 10^{-12} A) below the $V_G < -1$ V range, sharply increases at 0 to 5 V (from 10^{-12} to 10^{-6} A) and saturates at

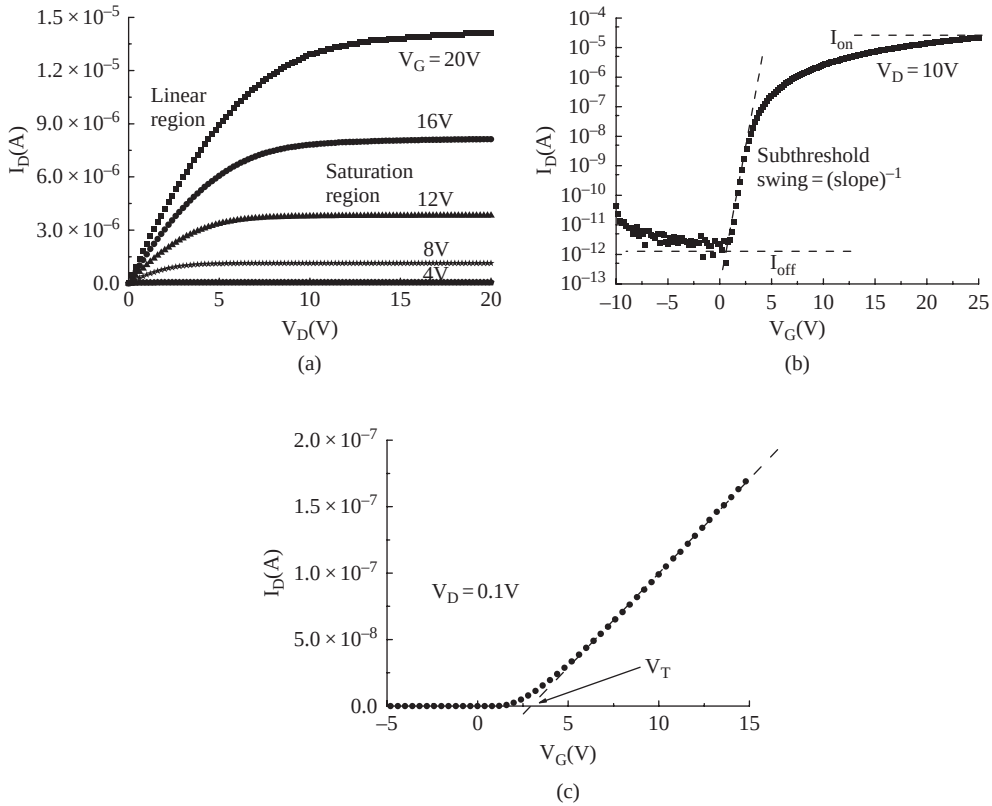


Figure 3.15 (a) Output characteristic, (b) transfer characteristic and (c) I_D versus V_G at a small V_D value of an a-Si TFT. (Data provided by Prof. I-Chun Cheng, National Taiwan University.)

about 10^{-5} A. From the transfer characteristic, one can obtain the on/off ratio of a TFT, which is the ratio of the maximum to minimum measurable current. Typically, values of 10^6 to 10^8 are achievable for an a-Si TFT. A higher on/off ratio is preferred since a higher ‘on’ current can provide better driving capability and lower ‘off’ current means lower leakage current. As is evident from Equations (3.17) and (3.18), increasing the mobility value effectively helps to improve the ‘on’ current, such as is achieved by using poly-Si rather than a-Si. However, due to the increase of the grain size, the surface roughness of poly-Si is greater than that of a-Si, which also increases the ‘off’ current. Hence, one may not achieve a higher on/off ratio when using poly-Si rather than a-Si, although poly-Si exhibits a higher carrier mobility. To quantitatively determine the V_T value, it is easier to plot the I_D – V_G curve using a linear scale. Figure 3.15(c) shows the I_D – V_G curve for a small value of V_D of 0.1 V in the low I_D region. Here, the TFT operates in the linear region due to the small V_D value. Equation (3.17) can be written approximately as

$$I_D \sim (\mu_n C_i) \left(\frac{W}{L} \right) (V_G - V_T) V_D, \quad (3.19)$$

and we can assume that the V_D^2 term in equation (3.17) is very small and can be neglected. We can find V_T from the x -intercept since $I_D = 0$ at $V_G = V_T$; this is the voltage required to switch on this TFT. Once V_T is obtained, one can fit the mobility value for such a device from Equations (3.17) and (3.18). Above V_T , there would be a significant current passing through the channel. In contrast, one can define a

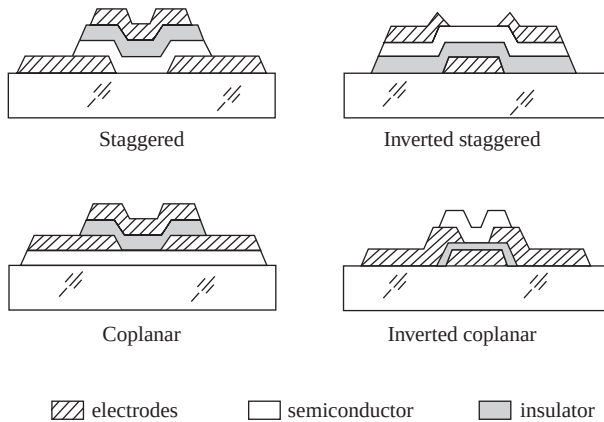


Figure 3.16 Different configurations of TFTs.¹³ (Source: Powell, M.J. (1989) The physics of amorphous-silicon thin-film transistors. *IEEE Trans. Electron Dev.*, **36**, 2753. © 1989 IEEE.)

subthreshold swing from Figure 3.15(b). This is the inverse of the slope of $\log(I_D)$ versus V_G , in terms of V/decade. This parameter indicates how much voltage is needed to switch the TFT on and off. A smaller subthreshold swing is preferred since this results in higher speed and lower power consumption.

Typical TFTs can be categorized as normal or inverted structures, depending on whether their gate is on the top or bottom, respectively. Another classification depends on whether the drain/source and gate are on the same or opposite sides; these are called coplanar or staggered structures, respectively. Hence, there are basically four different kinds of TFT structures, which are shown in Figure 3.16. Different structures may be the result of different fabrication procedures and may result in different device performance. Typically, a-Si TFTs use the inverted staggered structure configuration because it makes them easy to fabricate and gives them better electrical characteristics. The a-Si channel is sensitive to photons of the external ambient that mainly illuminates from the bottom side in a display system: an inverted structure can shield the device from this light by virtue of the gate metal. Also, because of the laser irradiation recrystallization process to convert a-Si to poly-Si, a flat and continuous silicon thin film without other layers beneath is a better choice for low-temperature poly-Si (LTPS) TFTs. Hence, these devices typically make use of normal planar structures.

3.5 Passive matrix and active matrix driving schemes

To drive an LCD or OLED display, passive matrix (PM) and active matrix (AM) driving techniques are commonly used.^{14, 15} For a PM LCD, due to the capacitor characteristics of the liquid crystal (LC) layer, a voltage applied to a selected pixel inevitably affects the neighboring pixels and degrades the contrast of the display, which is called crosstalk.¹⁶ Each row of a PM LCD or OLED display is sequentially active with a high frequency, and the human eye regards it as a planar frame rather than line scanning due to the persistence of vision. Since only one row can be selected and displayed at a time, the display time for a single row decreases with increasing number of rows, which limits the display size and resolution. In contrast, by using TFTs in an LCD or OLED pixel, the turn-on/turn-off and different greyscales can be controlled independently: this is called AM driving.

Figure 3.17 shows the operation of a PM LCD. Electrodes in a stripe configuration are placed on two glass substrates. Stripes on the bottom and top glass substrates are aligned perpendicularly to work as column and row electrodes of the PM LCD, and each crossed section is a pixel region. LC material is filled between the two glass substrates, thus together they can be regarded as a capacitor. To display a

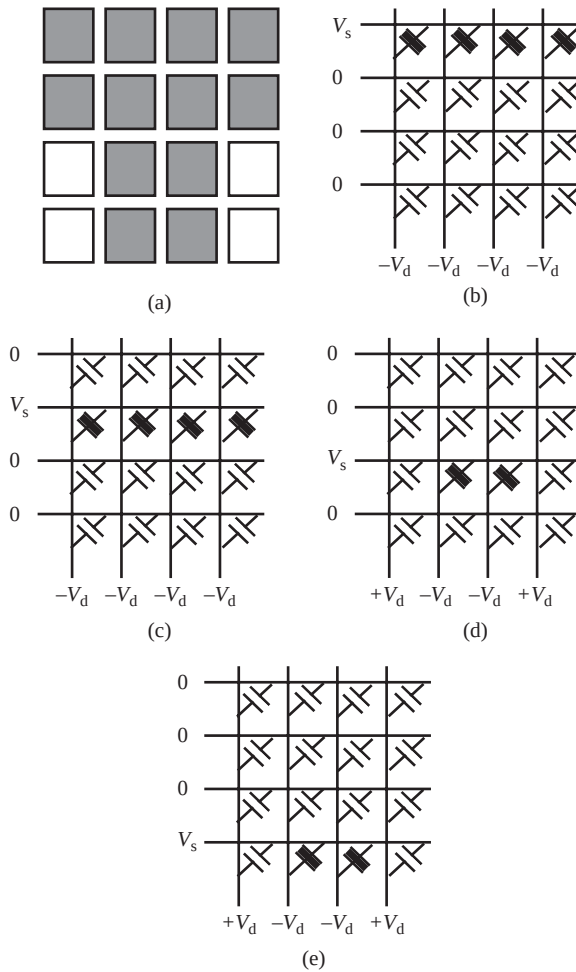


Figure 3.17 (a) Image displayed on a PM LCD, and the voltage at (b) first, (c) second, (d) third and (e) fourth time slots at each row and column.

‘T’ in a 4×4 LCD, the first row is first selected with a pulse voltage V_s for the first time slot, then the driving voltages from columns 1 to 4 are applied with $-V_d$, resulting in a voltage difference of $V_s + V_d$, and the left row lines 2 to 4 are applied with 0 V in root-mean-square (RMS) average (V_{rms}), so their voltage differences in the first time slot are V_d . Contrary to the V_D and V_S in Eq. 3.17 and 3.18, V_d and V_s here do not mean voltages at sources and drain, respectively, because it is PM driving without TFT. On the other hand, it represents voltages at data and scan lines. Then in the second time slot, the voltage on the row 1 electrode is reset to 0 V_{rms} , and the scanning voltage V_s is applied on row 2, and driving voltages for columns 1 to 4 are set at $-V_d$; hence only those pixels in row 2 have a voltage of $V_s + V_d$ and other pixels still experience a voltage difference of V_d . For the third time slot, scanning voltages for row 3 are V_s , but driving voltages for columns 2 and 3 are $-V_d$, and for columns 1 and 4 are $+V_d$; thus the voltage differences on pixels (3, 2) and (3, 3) are $V_s + V_d$, and voltages $V_s - V_d$ ($V_s + V_d$ for on, $V_s - V_d$ for off) are applied on pixels (3, 1) and (3, 4). In this slot, other pixels have voltages of either

$-V_d$ or $+V_d$. A similar driving scheme is then applied for row 4 in the next time slot. Generally, the LCs will respond to the RMS value of the voltages they experience.

For a PM LCD with N row lines, if one row is selected, a voltage of V_s is applied on that row line to select all the pixels there, and V_d or $-V_d$ from the column line is then used to turn each pixel on or off. But neighboring pixels in the same column will also be affected by the voltage from the same column line. As a result, for a whole frame scan, the on pixel has a voltage of $V_s + V_d$ only for $1/N$ frame time, and has a voltage of V_d or $-V_d$ for the remaining $(N - 1)/N$ frame time. Similarly, for a whole frame, the off pixel has a voltage of $V_s - V_d$ only for $1/N$ frame time, and V_d or $-V_d$ for the remaining $(N - 1)/N$ frame time. Since LCs respond to the RMS value of the receiving voltage, the RMS value of on or off pixels can be calculated from the above schemes:

$$V_{\text{on}}^2 = \frac{1}{N}(V_s + V_d)^2 + \frac{N-1}{N}V_d^2 \text{ and } V_{\text{off}}^2 = \frac{1}{N}(V_s - V_d)^2 + \frac{N-1}{N}V_d^2.$$

So, on average, different pixels of a display can be made to achieve on or off states by setting appropriate V_s and V_d values. Also, the difference between V_{on} and V_{off} of this display is related to the number of rows N . For a practical LCD with a set voltage–transmittance curve, the difference between V_{on} and V_{off} cannot be zero; thus the maximum row number of the display is limited.

Figure 3.18 shows the operation of a PM OLED. Here, we take a diode to illustrate the OLED display. As in the LCD case, to display a ‘T’ in a 4×4 OLED display, the first row is selected with a low voltage. The four OLEDs in the first row are biased at high voltage when the column lines are turned on. Then, for the next time slot, the second row is biased with low voltage, and so forth. The advantages of the PM OLED include ease of fabrication and low cost. However, since each row is

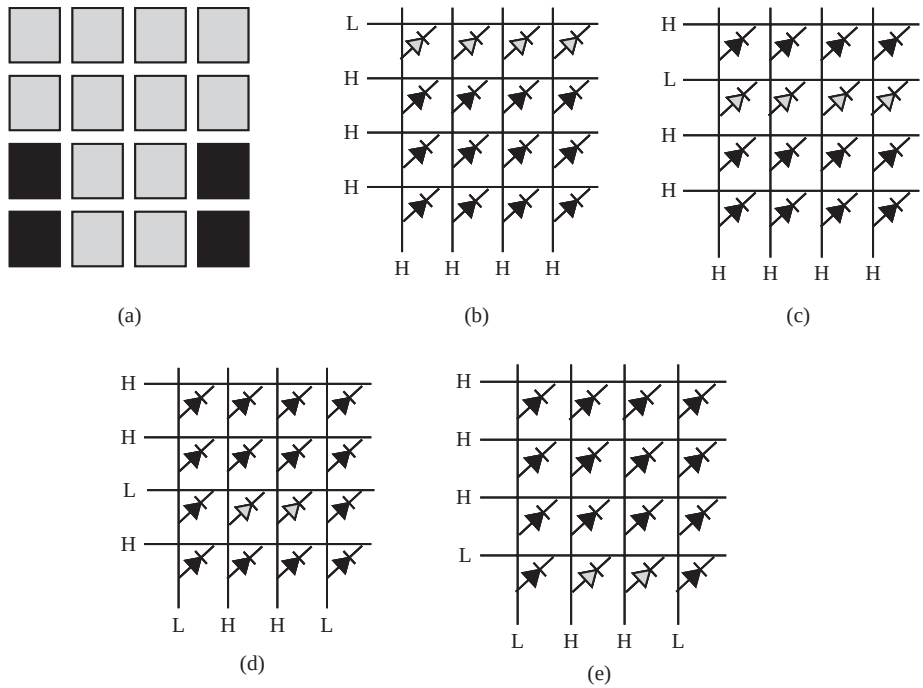


Figure 3.18 (a) Image displayed on a PM OLED, and the voltage at (b) first, (c) second, (d) third and (e) fourth time slots in each row and column.

selected at a short time slot, the average luminance is the peak luminance over the number of rows. When the number of rows increases, the peak luminance needs to be very high, which shortens the device lifetime.¹⁷

There are some differences between OLEDs and LCDs as regards PM driving. For an OLED, each individual pixel has a fast turn-on time that is close to or faster than each slot time; thus the luminance for each pixel reaches a peak from this turn-on slot, and is then averaged over all the rows (or scanning time). In contrast, for an LCD, the LC response time is usually slower than the turn-on slot time; thus, for a single scanning slot with high voltage, there might not be enough time to respond to reach peak transmittance before the voltage is reset at the next time slot. But LCs will respond to the average RMS voltage value and output a transmittance according to this RMS value.

Each pixel in a single frame of a PM LCD and PM OLED has on and off states, which means it has two gray levels, 0 and 1. To realize more gray levels for PM displays, pulse width modulation (PWM) is usually applied as one of the common driving schemes. That is, the pulse width on a pixel is controlled to obtain more gray levels. Due to the persistence of vision, the human eye receives the time-average brightness. As shown in Figure 3.19, a frame with two gray levels is divided into three time intervals which are displayed sequentially to obtain four gray levels. When three time intervals are all dark, the resulting screen is also dark (gray level 0). However, if one of the three is bright, then the screen looks dark gray (gray level 1). On increasing the number of bright time intervals, one can perceive that the ultimate color becomes light gray (gray level 2) and then white (gray level 3). Hence, there are four gray levels now controlled by the pulse width. For PM LCDs, due to the slow response of LCs, blurring of the image may occur when displaying moving pictures.

For a display with a greater number of rows (higher resolution or larger size), the AM driving technique using TFTs is typically used. Figure 3.20 shows the equivalent circuit of an AM LCD. Only one scan line is selected at a time. Once the scan line is selected, the TFT is switched on; then voltage from the data line can be fed to charge both the LC and the storage capacitor. When the scan line is not selected and the TFT is switched off, the LC pixel can still be biased, since the voltage is held by the storage capacitor. This is also called a hold-type display. Usually an extra capacitor is connected in parallel to the LC to improve the retention characteristics. This is called a storage capacitor. Unlike the PM LCD, where the driving voltage is related to the number of rows, the AM LCD is a hold-type display and crosstalk is much weaker. The gray levels can be controlled independently for each pixel; this is achieved by applying a different V_D directly from the data line.

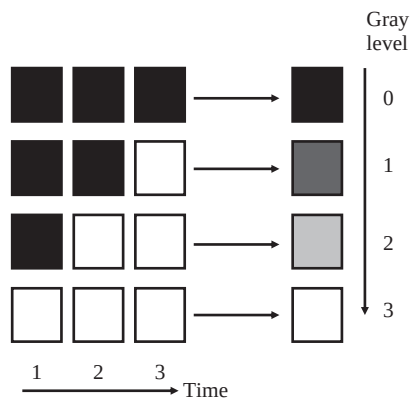


Figure 3.19 Four gray levels achieved by PWM.

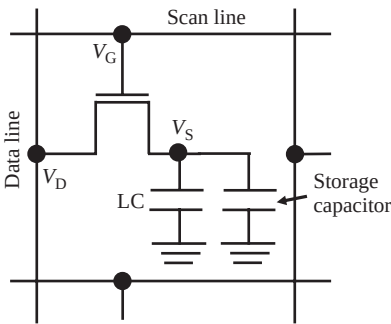


Figure 3.20 Equivalent circuit of an AM LCD.

Example 3.2

For the equivalent circuit shown in Figure 3.20, find the charging time of the LC, i.e. V_S , from 0 to $4.5 V_{rms}$ with $V_D = 5$ and $9 V_{rms}$, respectively. V_D is always kept at 5 and $9 V_{rms}$, while V_G is a step function which jumps from 0 to $20 V_{rms}$ at $t = 0$. There is no charge stored at LC ($V_S = 0 V_{rms}$) for $t < 0$. Timing diagrams of V_G and V_D are shown in Figure 3.21. When $V_G = 0 V_{rms}$, the leakage current can be neglected (open circuit, $R_{off} = \infty$). When $V_G = 20 V_{rms}$, the TFT can be replaced by a resistor with $R_{on} = 5 M\Omega$. The capacitance of the LC layer (including storage capacitor) is $C_{LC} = 3 pF$.

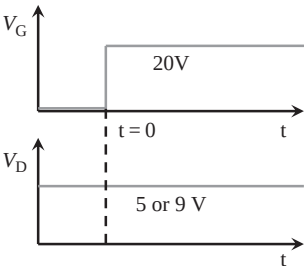


Figure 3.21 Timing diagram of V_G and V_D of Example 3.2.

Answer. Figure 3.22 shows the equivalent circuit when $V_G = 0$ and $20 V_{rms}$. When the gate is open at $t = 0$:

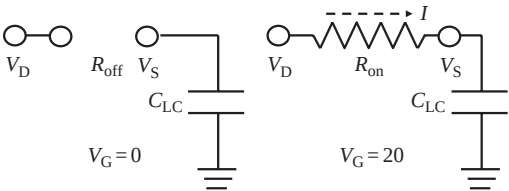


Figure 3.22 Equivalent circuit for (a) $V_G = 0$ and (b) $V_G = 20 V$.

(continued)

$$I = \frac{V_D - V_S}{R_{on}}, \quad (3.20)$$

$$I = C_{LC} \frac{dV_S}{dt}. \quad (3.21)$$

Equating Equations (3.20) and (3.21) yields

$$\frac{V_D - V_S}{R_{on}} = C_{LC} \frac{dV_S}{dt} \quad (3.22)$$

or

$$R_{on} C_{LC} \frac{dV_S}{dt} + V_S = V_D. \quad (3.23)$$

Solving this differential equation, we obtain

$$V_S = V_D [1 - \exp(-t/\tau)], \quad (3.24)$$

where

$$\tau = R_{on} \times C_{LC}. \quad (3.25)$$

Hence, for V_S , from 0 to 4.5 V_{rms} with $V_D = 5$ and 9 V_{rms} , the charging times are 34.5 and 10.4 μs , respectively. In reality, the gate signal is only applied for a very short time in a TFT LCD. For example, for a panel with resolution of 1024×768 at a frame rate of 60 Hz, the V_G duration is only $1/(60 \times 768) = 21.7 \mu s$. Hence, a suitable V_D value is needed to achieving the desired V_S at such a short time slot. As shown in Example 3.2, if $V_D = 5 V_{rms}$, the charging time from 0 to 4.5 V_{rms} is even longer than the duration of V_G , which results in insufficient charging of the LC cell.

The AM driving method of an OLED is similar to that of an LCD. However, since an OLED is a current-driven device, rather than a capacitor as in the case of the LCD, a more complicated circuit is needed for an AM OLED display. Figure 3.23 shows the equivalent circuit of an AM OLED pixel. Typically, at least two TFTs are required, which are marked as the address and drive TFTs. When the electrical pulse is scanned to a certain row, the address TFT is switched on. To light on a particular pixel in this row, data line is selected, and the current provided by the power line passes through the drive TFT onto the OLED. Note that there is a capacitor, which can hold the voltage when the scan line is deselected, which means that the OLED keeps emitting light when the row is not selected. Hence, the peak luminance of AM OLEDs

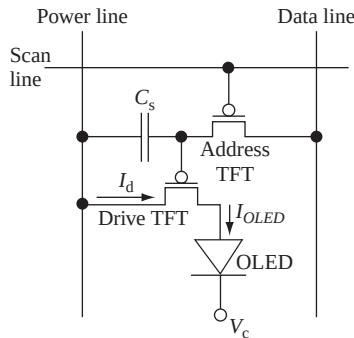


Figure 3.23 Equivalent circuit of an AM OLED with a two-transistor and one-capacitor configuration.¹⁵

does not need to be as high as that of PM OLEDs to achieve the same average brightness for each frame, which also extends the operation lifetime and makes a larger size display possible. This kind of pixel design is typically called a two-transistor and one-capacitor configuration. Here, the requirements for the address and drive TFT are quite different. The address TFT is used as a switch, and hence the on/off ratio is important. The drive TFT is used to provide current to the OLED, and hence a high current density capability is required. For the drive TFT to provide an adequate current, a high mobility is typically required. From this viewpoint, the LTPS technique is more suitable for driving the OLED. However, the uniformity achieved using the LTPS technique is not as good due to the laser annealing process. Since the J - V characteristics of OLEDs follow space charge limited current or trap charge limited current, described in Chapter 7, the current density varies greatly, even with a small driving voltage difference. Therefore, more than two TFTs are sometimes used to compensate for the nonuniformity of the LTPS TFTs and ensure a stable current density. To achieve different gray levels of the AM OLED, voltage modulation from the data line or PWM can be applied. The voltage modulation scheme in AM OLEDs is similar to that in AM LCDs. However, due to the steep luminance-voltage curve of OLEDs, it is not easy to control the gray levels precisely and uniformly. In the case of PWM driving, due to the higher frame rate, the power consumption is higher and the control system is more complicated.

3.6 Non-silicon-based thin-film transistors

In this section, we will introduce two kinds of TFTs where the active layer consists of organic molecules and ZnO-based materials. Organic TFT (OTFT) can be fabricated with a low temperature deposition and a solution process, which is less complex compared with conventional Si-based technologies. In addition, due to the mechanical flexibility of organic material, OTFT can be used as the backbone of the flexible display, and this has the benefit of being rugged, thin and lightweight.¹⁸ Also, it is potentially of low cost due to the possibility of using the roll-to-roll process. When fabricating a flexible display on a plastic rather than a glass substrate, one important issue arises concerning the durability of the substrate.

Several methods can be used to form the organic thin film. For organic materials with lower molecular weight which can be evaporated or sublimated, one can heat up materials in a vacuum chamber to deposit the organic thin film on the substrate. Pentacene is one of the most common low molecular weight organic materials used for p-channel TFTs. The molecular structure of pentacene is shown in Figure 3.24(a). The mobility value of OTFTs is varied by varying many parameters, such as molecule stacking configuration, surface morphology and grain size. By controlling the fabrication parameters such as deposition rate and substrate temperature, one may obtain pentacene with a larger grain size. The mobility of pentacene-based TFTs can be as high as $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is comparable to that of a-Si TFTs.¹⁹ By growing a single-crystal organic thin film such as rubrene (the molecular structure of which is shown in Figure 3.24(b)), the mobility value of an OTFT can exceed $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²⁰ Also, one can dissolve the organic materials in certain solvents. This makes it possible to spin-coat, inkjet-print, stamp or imprint the solution on the

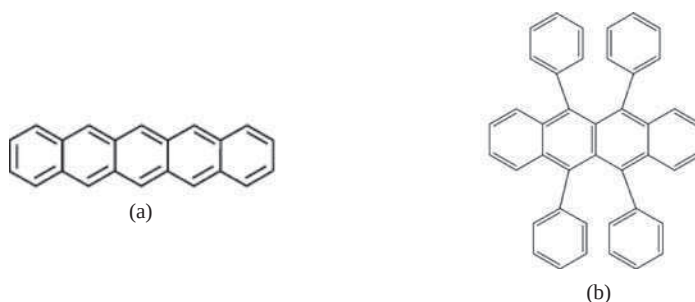


Figure 3.24 Molecule structures of (a) pentacene and (b) rubrene.

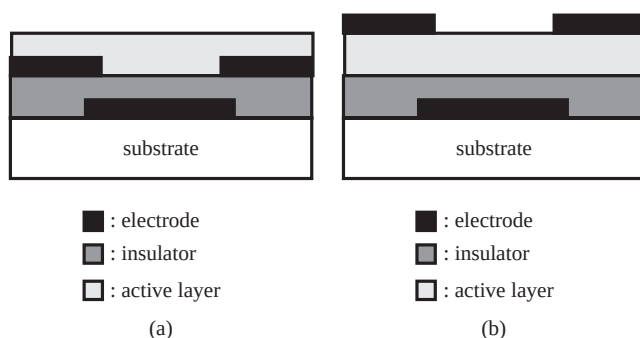


Figure 3.25 Device configurations of OTFTs: (a) bottom contact and (b) top contact.

substrate.²¹ After vaporization of the solvent, the organic material is left as a thin-film structure. Details of the fabrication of organic thin films are discussed in Section 7.5.3.

Many OTFTs are sensitive to environmental species, such as water and oxygen.²² This means that it can be difficult to obtain a stable device for display applications. During device fabrication, formation of the organic thin film is typically directly followed by a passivation process, which is used to avoid attack by environmental species. Figure 3.25 shows two common device configurations.²³ Both are of the inverted structure type, since the insulator must be formed before the organic thin film. For a bottom contact device, the organic layer is deposited at the top of the device. Drain, source, gate and insulators can be defined by conventional photolithography which provides a high resolution (less than 1 μm). For a top contact device, the organic material is formed first, followed by drain and source electrode evaporation through a shadow mask. The resolution is limited to several tens of micrometers in this configuration. As regards device performance, OTFTs with a top contact typically exhibit a superior performance compared to bottom contact types due to the larger contact area and lower contact resistance. Typically, a molecular thin film exhibits a much lower mobility value than semiconductor materials with covalent bonds, which means the electric current provided by OTFTs is typically smaller than that of a-Si and poly-Si based TFTs. It is also difficult to change the carrier concentrations of the molecules by intentionally doping, which limits the flexibility of device design. Also, the long-term stability under operation and storage is still an issue for OTFTs.²⁴

Due to the light-sensitive characteristics, a light shield is needed for the TFT region, which limits the aperture ratio of a display. By using high bandgap semiconductors, such as zinc oxide (ZnO), there is little absorption in the visible region. It is also possible to fabricate a light-insensitive TFT, called a transparent TFT (TTFT), which can greatly increase the aperture ratio.²⁵ Figure 3.26 shows the device structure and transmission spectrum of a ZnO-based TFT. Here, all the electrodes (gate, drain and source) are of transparent indium tin oxide (ITO). The insulator is made of aluminum titanium oxide (ATO), which is also transparent. As shown in Figure 3.26(b), the average transmission over the visible range at the channel and source/drain region is about 75%.

Another advantage is the high mobility (up to 20 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$), which is much higher than that of a-Si. Fabrication techniques for ZnO thin films include sputtering or pulsed laser deposition. These are physical vapor deposition (PVD) techniques, and different from the CVD system for a-Si growth.²⁶ Unlike a-Si, the amorphous phase is preferred for TTFTs since crystallization results in a high roughness and large leakage current, which reduces the on/off ratio of TTFTs. It is interesting that the mobility value does not differ much for ZnO-based materials in the crystalline and amorphous phases. In such materials, electrons mainly propagate along the large metal atom, which has a good wavefunction overlap in both crystalline and amorphous phases. To obtain good performance, it is also possible to incorporate other metal oxides into ZnO, such as In_2O_3 and Ga_2O_3 (IGZO).²⁷ There are some requirements for material

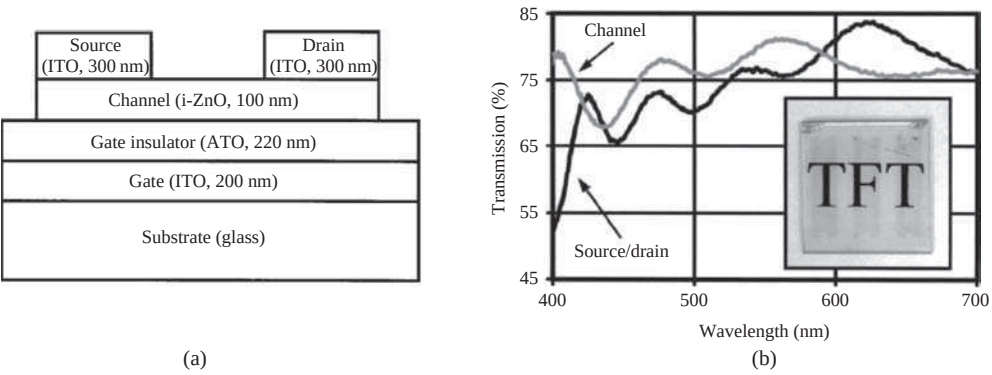
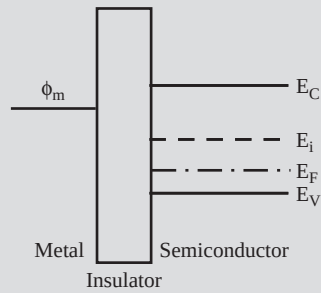


Figure 3.26 (a) Device structure and (b) transmission spectra of a TTFT.²⁵ (Reprinted with permission from Hoffman, R.L., Norris, B.J. and Wager, J.F. (2003) ZnO-based transparent thin-film transistors. *Appl. Phys. Lett.*, **82**, 733. Copyright (2003), American Institute of Physics.)

selection. The materials should (1) tend to form an amorphous phase during PVD, (2) have a high carrier mobility and (3) exhibit low carrier concentration for reducing the off current. By reducing the process temperature, TTFTs can also be fabricated on flexible substrates.

Homework problems

- 3.1 A Si wafer is doped with phosphorus at 10^{17} cm^{-3} . The wafer thickness is $350 \mu\text{m}$. Assuming the shape of the Si wafer is a complete circle with four inches in diameter. Also assume the electron current is much higher than the whole one with electron mobility $\mu_n = 700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Find the current when applying 10 V at both sides of this wafer.
- 3.2 GaAs and silicon have electron effective masses of $0.07m_0$ and $0.19m_0$, respectively, at the bottom of the conduction band. What is the physical meaning of the fact that the ‘effective’ mass of an electron in a semiconductor is less than the ‘real’ mass of a free electron? Which material exhibits a steeper $E\text{--}k$ curve at the bottom of the conduction band? Why?
- 3.3 Band diagram of an MIS device is shown below. Is V_m (voltage applied to the metal) positive, negative, or zero under flat band condition (V_{FB})? Draw the band diagram under a short circuit condition ($V = 0$).



- 3.4 For a TFT with $V_T = 1 \text{ V}$, $W = 50 \mu\text{m}$ and $L = 10 \mu\text{m}$, $\mu_n = 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $C_i = 15 \text{ nF cm}^{-2}$. Calculate the drain current at $V_G = 10 \text{ V}$ and $V_D = 0.1 \text{ V}$. Repeat the calculation for $V_G = 20 \text{ V}$ and $V_D = 20 \text{ V}$.

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6

Light-emitting diodes

6.1 Introduction

The operation principle of light-emitting diodes (LEDs) is to inject electrons and holes into a single-crystal semiconductor where carriers recombine and generate photons. The emission wavelength of the LEDs depends on the material selection, active-layer design and device structure, and can cover the whole visible range. Although electroluminescence (EL) in a semiconductor (SiC) was first observed in the early twentieth century,¹ the commercial realization of visible LEDs started around 60 years later.

For higher recombination rate, a direct bandgap material (i.e. the minimum of the conduction band and the maximum of the valence band coincide at the k -space) is preferred. In the 1960s, visible LEDs emitting a red color were realized by using a GaAsP active layer on a GaAs substrate.² One of the major problems of this system arises from the lattice mismatch between the GaAs (lattice constant = 5.65 Å) and GaAsP (lattice constant = 5.45 Å) which results in misfit dislocation and, in turn, to an increase in the nonradiative recombination rate. Emission wavelengths of GaAsPLEDs can be blue-shifted by increasing the percentage of phosphorus. However, a direct–indirect transition occurs when the phosphorus mole fraction increases to 50 %, which results in an efficiency decrease. By incorporating some isoelectronic impurities (N and Zn:O) into indirect bandgap materials (such as GaP or GaAsP), which form a trap level inside the forbidden bandgap, a shorter emission wavelength (orange, yellow or even green) of LEDs was achieved in the 1970s.³ Another material system is AlGaAs on GaAs substrate (1980), which has the advantage of low lattice mismatch since the lattice constants are nearly the same for AlAs (5.66 Å) and GaAs (5.65 Å).⁴ Hence, a high-quality crystalline epitaxial film can be obtained for reducing the nonradiative recombination rate. Also, the layer structure can be engineered (such as heterojunction and quantum well) easily for better carrier confinement and fine tuning of the emission wavelength due to the lattice-matched condition. On increasing the aluminum concentration, the emission spectrum shifts towards shorter wavelengths. However, a direct–indirect transition occurs at 621 nm with Al = 45 %, which limits the AlGaAs/GaAs LED to operation only at the red emission region. Then, in 1990, the quaternary alloy InGaAsP was introduced with the advantages of: (1) lattice matched to GaAs by tuning the Al/Ga ratio and (2) shorter direct–indirect transition wavelength (555 nm; yellowish green) than GaAsP and AlGaAs systems, which is currently the mainstream of the ‘long-wavelength’ region (red, orange and yellow) of visible LEDs.⁵

GaN, InGaN and AlGaN (III nitrides) are other material systems, which cover the shorter wavelengths of the visible spectrum from ultraviolet (UV) and blue to green. Two major problems of these material

systems arise from the lack of a lattice-matched substrate and the difficulty in achieving p-type doping. By pregrowth of a buffer layer (e.g. AlN or GaN) at low temperature, it is possible to form an epitaxial nitride film on the lattice-mismatched substrate sapphire (Al_2O_3).⁶ Acceptors (which should act as p-type dopants) in nitride material are easily passivated by the hydrogen atoms introduced during epitaxial film growth. Hence, a high-temperature annealing under nitrogen ambient is needed to activate the acceptors and achieve an ‘effective’ p-type nitride material.⁷ For generating white light, two- or three-color mixing is needed. Typical approaches include: (1) all-semiconductor method by using different color LEDs and (2) down-conversion materials (such as phosphors) optically pumped by short-wavelength LEDs (UV or blue). Figure 6.1 shows the evolution of LED performances over time. We can see that the power efficiencies of LEDs have made a huge progress over the last several decades and are already higher than those of incandescent and fluorescent lamps.⁸

The requirements for achieving high performance from a LED,⁹ are: (1) inject and transport the carriers into the active layer for recombination without injection barriers and with little ohmic loss, (2) have a much higher radiative than nonradiative recombination rate and (3) couple the light out of the device efficiently. A high resistance of the semiconductor results in higher voltage and lower efficiency. Ohmic contact, rather than Schottky barrier, is needed for efficient carrier injection. Hence, a p–n diode structure with low resistance is preferred for LED applications. Since the radiative recombination process in LEDs is of Langevin type, the recombination rate distribution is proportional to the product of the electron and hole concentrations in the spatial domain. Hence, it is needed to confine carriers in the active region by using heterojunction, electron blocking layer, quantum well, quantum wire and quantum dot structures.

Once electron–hole pairs recombine, the energy may relax radiatively by generation of photons or nonradiatively by generation of heat. A single-crystalline semiconductor material is needed for LED applications since defects in semiconductors typically act as nonradiative centers which result in the decrease of the radiative recombination rate. The bandgap of the semiconductor material at the active layer determines the LED emission wavelength. Active layer design also plays an important role in emission spectra. Quantum well, quantum wire and quantum dot structures shift the emission wavelength from the bandgap to the quantized states which allows some flexibility in emission wavelength tuning. In addition, the densities of states of the low-dimensional structures (quantum well, wire and dot structures)

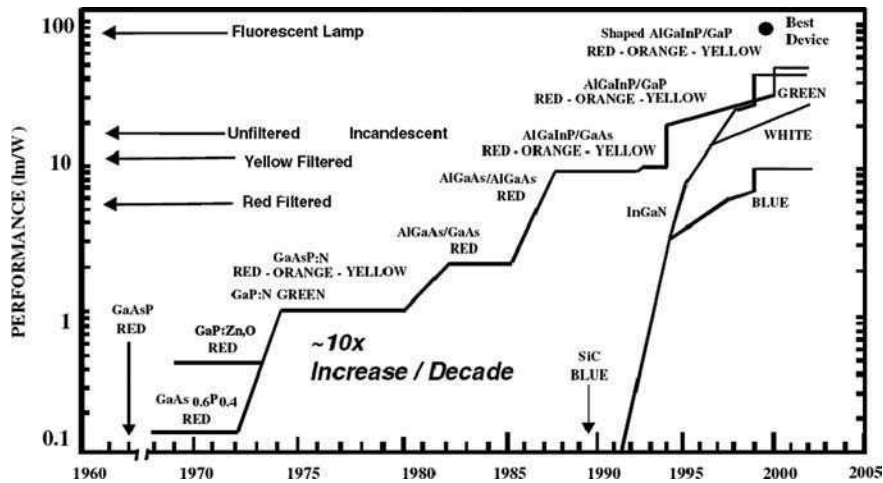


Figure 6.1 Power efficiencies of LEDs with time for long-wavelength (GaAsP, AlGaAs and AlInGaP) and short-wavelength (nitride) material systems.⁸

are different from that of the bulk material, which results in a change in the full-widths at half-maximum (FWHMs) and different temperature dependences.

Once photons are generated in the active layers of LEDs, the next stage is to radiate the photons out of the semiconductor material efficiently and be received by the human eye. Due to the spontaneous emission characteristics, the photon emission is isotropic, and may experience absorption (by defect states), reabsorption (band-to-band or free carrier) or scattering (by defects or interfaces) when propagating in semiconductor materials. If the substrate of the LED has a smaller bandgap (e.g. GaAs with $E_g = 1.424$ eV, corresponding to 870 nm in the near-infrared region) than visible light, the absorption from the substrate (theoretically 50 %) needs to be taken into consideration. When the photons propagate out of the semiconductor to the epoxy layer (which is used for packaging the LEDs), total internal reflection may occur due to the refractive index difference ($n = 3.5$ for semiconductor and 1.5 for epoxy). From a simple calculation using Snell's law, light with an incident angle from the semiconductor greater than a critical angle, about 25° in this case, cannot radiate to the epoxy layer. Those photons will reflect back into the semiconductor which may be absorbed by the defects or substrate, or propagate inside the semiconductor as waveguiding mode. To overcome these problems, many LED structures have been proposed: (1) surface texturing and reflectors can be used for destroying the waveguide effect and reflecting the light out; (2) a transparent substrate (e.g. GaP) can be employed to decrease the substrate absorption; and (3) the reflective metal electrode can be replaced by a transparent electrode (e.g. indium tin oxide, ITO).

Crystalline semiconductor layers with p-n structures and active regions of several micrometers are grown on single-crystal substrates, which is called the epitaxial process.¹⁰ Liquid phase epitaxy (LPE) and vapor phase epitaxy (VPE) are common techniques. One of the VPE systems with organo-metallic material sources, called metalorganic chemical vapor deposition (MOCVD), is one of the most popular methods for epitaxial growth. Many important material characteristics are determined in the epitaxial process, such as doping concentrations, doping profile, defect density and alloy compositions. Other criteria for LEDs with high power efficiency rely on suitable device design and fabrication techniques. Contact resistance between the electrode and the material should be as low as possible, which can be achieved by thermal annealing. Also, the layout of the contact should be optimized between the uniform current spreading and the high outcoupling efficiency. An etching process is needed to confine the current flow and increase the extraction efficiency. However, the etched face results in damage of the periodic lattice and increases nonradiative recombination. Suitable thermal annealing can effectively passivate dangling bonds. After the LED device is fabricated, suitable packaging is essential in real applications to: (1) protect the LED chips mechanically and environmentally, (2) improve the extraction efficiency and (3) provide a thermal path for high-power applications.

LEDs have many applications in the display industry. For traffic signals applications, LEDs have higher power efficiency and hence less power consumption than conventional filtered incandescent lamps. Longer lifetime is another important advantage which reduces maintenance costs. Electronic signage and huge displays over several hundred inches are another niche market for LED displays. Cold cathode fluorescent lamps (CCFLs) are conventional backlights for liquid crystal displays (LCDs); these lamps contain mercury and are harmful to the environment. The continuous spectrum also limits the color gamut of the LCD. White LEDs are promising candidates to replace CCFLs as the backlighting source of LCDs, due to their environmentally friendly characteristic, high color gamut, long lifetime and fast response. In addition to backlight units for LCDs, LEDs can also be used for general lighting due to their high power efficiency and long lifetime. Also, they are rugged due to their all-solid-state nature. The operation voltage is quite low (less than 5 V) as compared to other lighting technologies, which means LEDs are easier to drive and safer.

In this chapter, we first describe the material systems for visible LEDs. Then the electrical (diode) and optical (light-emitting) characteristics are introduced, which is followed by device fabrication. Finally, LED applications in displays are discussed.

6.2 Material systems

Material systems of LEDs determine the emission wavelength and radiative recombination efficiency. To emit photons with a desired wavelength, the active layer of an epilayer (which may be a binary, ternary or quaternary compound semiconductor) with a certain bandgap should be selected (a direct bandgap is much preferred). Then, a suitable substrate, which has to be lattice-matched to the epitaxial layer, is needed to reduce the nonradiative recombination rate.

Elementary semiconductors of group VI such as germanium, silicon and carbon (diamond) are indirect bandgap which is typically not suitable for LED applications. Figure 6.2 shows the curves of the bandgap and emission wavelength versus the lattice constant for III–V compound semiconductors. The points represent binary materials and the curves connecting the points represent ternary materials. Alloying two ternaries with one different atom (e.g. InGaP and InAlP) creates a quaternary material (e.g. InGaAlP), which is represented by the line ending at two ternary curves. We can see a general trend (although not universal) from Figure 6.2 that, on increasing the lattice constant, the bandgap decreases and the emission wavelength increases. Since the binding energy (which determines the bandgap) is greater for smaller atomic number, compound semiconductors consisting of ‘smaller’ atoms exhibit a larger bandgap. So, for example, the bandgap of GaAs is less than that of GaP which in turn is less than that of GaN since the atomic size is ordered as $\text{As} > \text{P} > \text{N}$. This is also generally true when replacing the group III material. For example, the bandgap of InN is less than that of GaN which in turn is less than that of AlN since the atom size is ordered as $\text{Al} < \text{Ga} < \text{In}$. Arsenic- and phosphorus-based compound semiconductors (e.g. GaP, GaAsP, AlGaAs, GaAs, InGaAsP) can be operated in the red, orange, yellow and even green region. To push the emission wavelength towards shorter wavelength, a smaller group V atom, nitrogen, is used.

The lattice constant between the substrate and epitaxial layer should be kept as low as possible. ‘Lattice mismatch’ is defined as the difference in lattice constant relative to the substrate, $\Delta a/a_0$, and should be typically as low as 0.1 % for obtaining a high-quality epitaxial layer. When the lattice constant between the epitaxial layer and the substrate is not matched, the residual strain results in deformation of the epitaxial layer, since this layer is much thinner than the substrate. If the accumulated strain is too high, dislocation occurs which increases the nonradiative recombination rate. Hence, lattice-match condition should be addressed carefully when selecting the material system. Common substrate materials are GaAs, InP and GaP. From Figure 6.2, one can see that GaP and InP exhibit extremely high and low bandgap conditions, respectively. At these two conditions, no suitable ternary and quaternary arsenic- and phosphorus-based

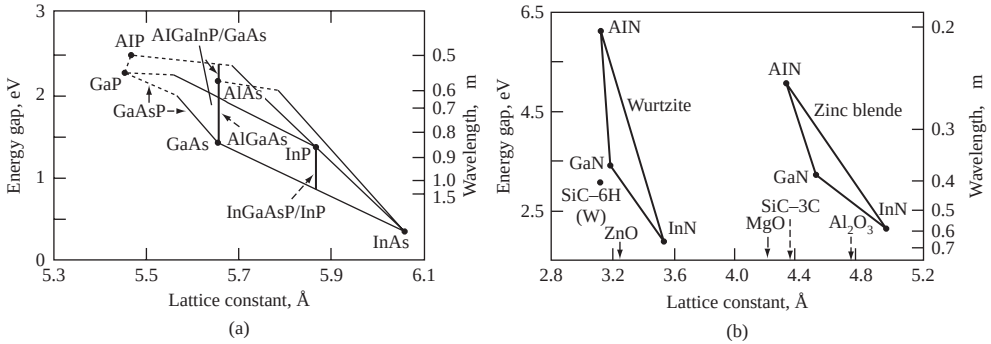


Figure 6.2 Bandgap and emission wavelength versus lattice constant for III–V semiconductors: (a) AlInGa–AsP and (b) AlInGa–N material systems.¹¹ (Reprinted from Mueller, G. (ed.) *Electroluminescence I, Semiconductor and Semimetals*, Vol. 64. Copyright (2000), with permission from Elsevier)

materials can be found to lattice-match to the substrate. GaAs is a suitable choice since it is lattice-matched to AlGaAs and $(\text{InGa})_{0.5}\text{As}_{0.5}\text{P}$. However, it should be noted that the bandgap of GaAs is 1.424 eV, corresponding to 870 nm in the infrared region, which means it absorbs visible light and, in turn, reduces the efficiency. For the nitride-based materials, no suitable III–V semiconductor materials could be found as the substrate, which delayed the development of short-wavelength LEDs until the 1990s. However, by pregrowth of low-temperature GaN with wurtzite structure on the lattice-mismatched substrate Al_2O_3 , high-efficiency green and blue LEDs can be fabricated.

As discussed in Chapter 3, semiconductors can be divided into direct and indirect bandgap materials, which are shown as the solid and dash lines, respectively, in Figure 6.2. Figure 6.3 shows schematic representations of the band structures of direct and indirect bandgap semiconductor materials. Direct bandgap means the minimum of the conduction band coincides with the maximum valence band at the momentum space. Since the momentum of photons is so small compared to electrons and holes, the optical transition is typically vertical in the band diagram shown in Figure 6.3. For the indirect bandgap condition, as shown in Figure 6.3(b), electrons accumulate at the lowest energy valley of the conduction band, which does not coincide with the maximum of the valence band. Hence, the momentum cannot conserve to emit a photon. ‘Phonons’ with low energy but large momentum should participate in the process for efficient light emission. Typically, direct bandgap materials exhibit much higher radiative recombination rates than indirect ones. On increasing the bandgap of As- and P-based materials, such as increasing the Al ratio of AlGaAs and $(\text{InGa})_{0.5}\text{Al}_{0.5}\text{P}$, direct–indirect bandgap transition occurs, which results in an efficiency reduction and limits the EL emission at longer wavelengths. Note that the transition of direct and indirect bandgaps is not an abrupt change in efficiency. Since the electrons tend to reside on

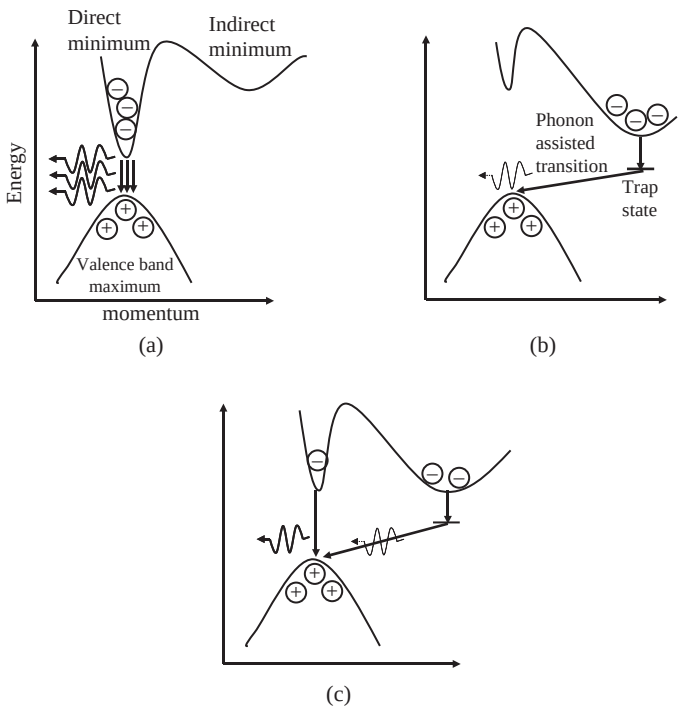


Figure 6.3 Energy versus momentum curves for semiconductors with (a) direct, (b) indirect and (c) near direct–indirect bandgaps.

the lowest energy determined by the Boltzmann distribution, some of the electrons occupy the states in the indirect valley when the energies between the direct and indirect bandgaps are close enough, although the semiconductor still has a 'direct' bandgap.

Hence, as shown in Figure 6.2(a), $(\text{InGa})_{0.5}\text{Al}_{0.5}\text{P}$ systems are latticed-matched to GaAs and are direct bandgap systems from red to amber regions, which they are suitable for visible LEDs in the long-wavelength region. The absorbing GaAs substrate can be removed and replaced by transparent GaP substrate after the epitaxial growth for further improving the external quantum efficiency. Moving from short to long wavelengths, InGaN with increasing In concentrations shows a high efficiency in the blue and green region. Hence, the blue-green III-N and amber-red III-P LEDs can cover the whole visible spectrum. However, although the luminous efficiency of the green InGaN LED is high, the internal quantum efficiency is low since the incorporation of In results in In clusters which results in the increase of nonradiative recombination.

Since the III-N and III-P materials are typically grown on different substrates (i.e. sapphire and GaAs, respectively), it is difficult to obtain emission of broad-band white light from a single LED chip. There are several ways for obtaining white light emission, such as (1) by assembling multiple LEDs in a module or (2) using phosphors which absorb the LED blue light and emit yellow light.^{12, 13} By using multiple LEDs, electrical and optical characteristics (such as efficiency, driving voltage and emission wavelength) of each device can be optimized individually. However, the cost is high and the device is bulky since more than a single LED is used. Also, after long-term operation, there may be color shift problems due to the different lifetime performances of different LEDs. For a phosphor-coated white LED, the efficiency is theoretically lower than that using the multi-LED technique since the emission wavelength of the phosphor is shorter than the absorption wavelength. Advantages of this technique include low cost, compact size and stable CIE coordinates. As discussed in Chapter 2, 'white' color means specific CIE coordinates located nearly at the center of the chromaticity diagram. However, as the light source of reflective displays, not only should the color of the LEDs be white, but also a high CRI value is important to reproduce the color as it is under the illumination of a blackbody radiator.

6.2.1 AlGaAs and AlGaInP material systems for red and yellow LEDs

As shown in Figure 6.2, GaAs is almost lattice-matched to AlAs, which means the ternary AlGaAs can be epitaxially grown on conventional GaAs substrate with low defect density. This also provides a large flexibility in designing epilayer structures, such as heterojunction and quantum well structures (Sections 6.3.4 and 6.3.5), for obtaining higher efficiency and desired emission wavelength.¹⁴ The energy gap of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ can be represented as¹⁰

$$E_g(\text{eV}) = 1.424 + 1.247x; \quad x < 0.45 \text{ (direct bandgap)}, \quad (6.1)$$

$$E_g(\text{eV}) = 1.9 + 0.125x + 0.143x^2; \quad 0.45 < x < 1 \text{ (indirect bandgap)}. \quad (6.2)$$

From the above equations, one can obtain that the crossover point of the direct-indirect bandgap happens at 1.985 eV, which corresponds to red emission of 624 nm. This limits AlGaAs in the red to infrared emission region although the internal quantum efficiency of the AlGaAs/GaAs system can be as high as 99 %. For obtaining shorter emission wavelength, III-P material systems are used in place of the III-As ones. To fit the lattice constant of the conventional GaAs substrate, a quaternary $((\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P})$ rather than ternary material is needed. The energy bandgap can be tuned from red to amber efficiently by varying the value of x , as shown in Figure 6.2. A more detailed expression of the lattice match condition for $(\text{Al}_x\text{Ga}_{1-x})_y\text{In}_{1-y}\text{P}$ on GaAs is

$$y = \frac{0.616}{1 - 0.027x}. \quad (6.3)$$

The value of y ranges from 0.516 to 0.525 and a value of approximate 0.5 is typically used. The bandgap of AlGaInP can be represented as¹⁵

$$E_g(\text{eV}) = 1.900 + 0.61x; \quad x < 0.58 \text{ (direct bandgap)}, \quad (6.4)$$

$$E_g(\text{eV}) = 2.204 + 0.085x; \quad 0.58 < x < 1 \text{ (indirect bandgap)}. \quad (6.5)$$

As we can see from Figure 6.2, the wide bandgap materials of GaP, AlP and their ternaries are indirect semiconductors. Hence, there is a crossover point from direct to indirect when x increase to 0.65, which corresponds to 2.3 eV or 540 nm (green emission). However, an efficiency decrease is observed when the wavelength is shorter than 590 nm due to the electrons accumulating at the indirect valley. So, AlGaInP material systems can provide an efficient emission range from red to amber. The refractive indexes of AlGaAs and AlGaInP systems are around 3.2 to 3.6, depending on the composition and wavelength. Typically, a smaller bandgap corresponds to a larger refractive index, which can be derived from the Kramers–Kronig relation.¹⁶

6.2.2 GaN-based systems for green, blue and UV LEDs

Typically, a single-crystal substrate of semiconductor is sliced from an ingot which is obtained by the melting and recrystallization process. For III–V compounds, group V materials exhibit much higher vapor pressure than group III for the same temperature, which increases the difficulties in fabricating substrates of III–V compound semiconductors compared with group IV silicon ingot fabrication. Also, in contrast to arsenic and phosphorus which still exist as solid phase at room temperature and 1 atm, nitrogen N is in the gas phase which means the vapor pressure of nitride is much higher, making it very difficult to obtain a nitride-based substrate. Due to the lack of a conventional semiconductor substrate that is lattice-matched to group III nitrides, insulating sapphire (Al_2O_3) is commonly used, although the lattice mismatch is as high as 16 % with GaN. Direct epitaxy of nitrides on sapphire substrate results in island (three-dimensional, 3-D) rather than planar (two-dimensional, 2-D) growth, combined with a high dislocation density, as shown in Figure 6.4. By introducing an AlN or GaN buffer layer grown at low temperature, a high-quality nitride epilayer can be obtained since it: (1) provides nucleation sites for epitaxial growth at the same crystal orientation which reduces the dislocation defect densities and (2) decreases the interfacial free energy between the substrate and the epitaxial layer which makes 2-D growth preferable.⁶

The bandgap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ ternary alloy is roughly given by

$$E_g(\text{eV}) = xE_{g,\text{InN}} + (1-x)E_{g,\text{GaN}} - (1-x)xb, \quad (6.6)$$

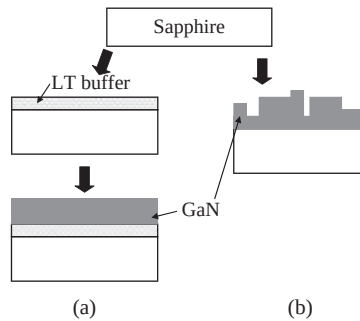


Figure 6.4 Growth of III-nitride (a) with and (b) without low-temperature buffer layers.

where $E_g\text{InN}$ and $E_g\text{GaN}$ are the bandgaps of InN and GaN, respectively. Reference bandgap values are 1.95 and 3.40 eV for InN and GaN, depending on the strain. Parameter b is called the bowing factor with a typical value of 1.00 eV.¹⁷ One can note that III–nitride semiconductors exhibit direct bandgaps for the whole range of compositions, from Equation (6.6). By tuning the x value from 0.15 to 0.45, UV to green LEDs can be realized. In nitride LEDs, indium atoms tend to form clusters in the epitaxial layer which results in some inevitable composition fluctuation.¹⁸ This can be observed from the spectral broadening of the photo- or electroluminescence which is called ‘alloy broadening’. With increasing indium concentration, the metallic indium clusters act as quenchers which results in low internal quantum efficiency of nitride LEDs for long wavelengths (green, yellow and red).

Lattice mismatch occurs not only between the substrate and the epitaxial layer, but also between different epitaxial layers. This results in strain between different layers (e.g. quantum well and barrier; Section 6.3.5) and hence a built-in potential inside the LED along the crystal growth direction. Such a piezoelectric field in nitride LEDs results in the spatial misalignment of the electron and hole wave functions.¹⁹ As shown in Figure 6.5, the emission spectra of the LED blue-shifts on increasing the pumping (optical or electrical) due the screening of the built-in electric field by the excess carriers. Similar to the III–P cases, it is also possible to apply quaternary AlInGa₂N to control the strain and fine tune the emission characteristics.²⁰ Magnesium is typically used for p-type doping of nitrides. Since NH₃ is used as the nitrogen source, the formation of high electronic conductivity Mg–H during epitaxial layer formation results in low hole concentrations. By using high-temperature annealing (>700°C) for dehydrogenation, it is possible to achieve a reasonable hole concentration and resistivity for LED (or even laser diode) applications.²¹

Example 6.1

Determine the composition of In_{*x*}Ga_{1–*x*}N in the active layer with emission wavelengths at 550 and 450 nm for green and blue LEDs, respectively.

Answer. For green and blue with emissions at 550 and 450 nm:

$$E_g(\text{eV}) = \frac{1240}{550(\text{nm})} = 2.2545; \quad E_g(\text{eV}) = \frac{1240}{450(\text{nm})} = 2.7556.$$

The x values of ternary alloy In_{*x*}Ga_{1–*x*}N can be calculated from Equation (6.6):

$$\text{In}_x\text{Ga}_{1-x}\text{N}(550\text{nm}): E_g(\text{eV}) = \frac{1240}{550(\text{nm})} = 1.95x + 3.4(1 - x) - x(1 - x); \quad x = 0.6291$$

$$\text{In}_x\text{Ga}_{1-x}\text{N}(450\text{nm}): E_g(\text{eV}) = \frac{1240}{450(\text{nm})} = 1.95x + 3.4(1 - x) - x(1 - x); \quad x = 0.2997.$$

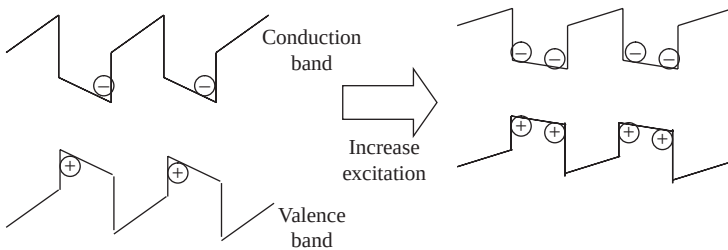


Figure 6.5 Band structure shift of III–nitride under excitation.

6.2.3 White LEDs

To generate white light from LEDs, there are at least two different techniques, as summarized in Table 6.1. The first is by using multiple LED chips. As mentioned before, since the integration of different substrates is difficult, the physical size of this white-light module cannot be too small. The second technique is to use the LED (blue or UV) to excite phosphors. This can be also distinguished from the ‘composition’ of the white light, also shown in Table 6.1. Due to the lack of broad-band emission from a single LED, white light consists of two, three or even more colors. From colorimetry, white light from a mixture of two colors exhibits the highest maximum attainable luminous efficiency (in terms of lm W^{-1}). However, for obtaining a high CRI value in light source applications, three or more colors that provide a broad-band emission are needed.

It is straightforward to mix emissions of two or more LEDs with different wavelengths to obtain white light, following the colorimetric principles described in Chapter 2. The efficiency of this technique is typically higher than the LED pumping phosphors method since wavelength conversion is not needed which wastes energy. However, more LED chips means a higher cost and larger size. Due to the nonlinearity of the light–current relation of different LEDs, the color of this white light is not stable over different current injection. With increasing temperature, LED intensity decreases and spectrally red-shifts which also results in a color shift of the white light. After long-term operation, the different operation lifetimes of the LEDs also result in color change. For the two-color mixing technique, LEDs of two complementary colors (typically blue and yellow) are used. Since the sensitivity of the human eye is highest at 555 nm and decreases on both sides at the photopic region, it is reasonable that there exists an optimized value for the maximum attainable luminous efficiency of two complementary colors with different wavelengths, which can be derived from color science and engineering, as described in Chapter 2. With longer or shorter wavelength combinations, there is a decrease of the maximum attainable luminous efficiency, which implies two-color mixing with narrow emission spectra is the most efficient way to generate white light. Under the assumptions of (1) a combination of two monochromatic complementary colors and (2) 100 % electrical to optical energy transfer, the upper theoretical limit of the white light is over 400 lm W^{-1} . Hence, such a white light source is very suitable for ‘white’ display applications such as pedestrian traffic signals due to its low power consumption. However, it is not suitable for light source applications since the CRI value is typically low, due to the narrow spectra and two-color combination. To obtain a high CRI value, a broad-band emission is usually needed, which also implies a tradeoff between the CRI value and the efficiency. So, it can be expected that the maximum attainable luminous efficiency for three-color mixing is somewhat lower but with higher CRI value, which is more suitable for lighting applications. It is also possible to increase the number of LED colors (four or five) to obtain larger gamut values, but the tradeoff is the low efficiency and high cost. Another important application for three-color LEDs is in LCD backlights. For this application, LEDs with narrower emission spectra are preferred for larger color gamut values.

Another common way to generate white light is by using a blue or UV LED to pump phosphors. Such a method is relatively simple and of low cost since only a single LED is needed. Besides, the phosphors can be coated during the encapsulation process inside the LED package. Hence, small physical dimensions can also be achieved. Since the lifetime of conventional phosphors is long, the color stability of this type of white LED is also very good. However, compared with the multi-LEDs scheme, this technique has an

Table 6.1 White light generation techniques.

	Multiple LEDs	LED pumps phosphor
Two-color mixing	Y + B LEDs	B LED pumps Y phosphors
Three-color mixing	R + G + B LEDs	UV LED pumps white phosphors (RGB mixture)

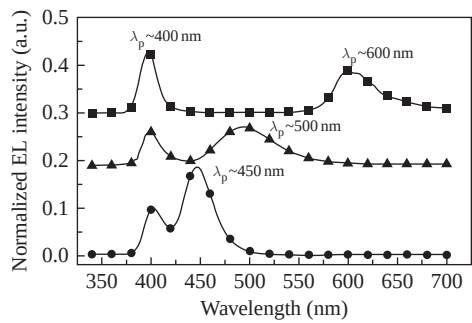


Figure 6.6 Emission spectra of UV radiation ($\lambda_p \approx 400$ nm) pumping (a) red ($\lambda_p \approx 600$ nm), (b) green ($\lambda_p \approx 500$ nm) and (c) blue ($\lambda_p \approx 450$ nm) phosphors.²² (Source: Sheu, J.K. *et al.* White-light emission from near UV InGaN–GaN LED chip precoated with blue/green/red phosphors. *IEEE Photon Technol. Lett.*, **15**, 18. © 2003 IEEE)

inevitable disadvantage of theoretically lower efficiency. As shown in Figure 6.6, the phosphor absorbs photons with higher energy in the UV region with a peak of 400 nm and emits lower energy photons at 600, 500 and 450 nm, for red, green and blue emissions, respectively.²² Typically, the internal quantum efficiency of the phosphor can be as high as 90 %, which means 90 photons are emitted per 100 photons absorbed. However, there is an energy loss between the photons absorbed and emitted, which is called the Stokes shift. In this case, the energy loss originating from the Stokes shift results in an efficiency decrease of 33.3, 20 and 11.1 % for red, green and blue emissions, respectively. Another possible energy loss arises from the light scattered by the phosphor which is reabsorbed by the LED chip, package and reflectors.

There are lots of ‘down-conversion’ materials which can absorb blue and UV light and generate photons with longer wavelength, such as organic dyes,²³ semiconductors²⁴ and nanocrystals.²⁵ However, there are some disadvantages for these materials, such as reliability issues and/or high cost. Typically, inorganic phosphors are commercially used as wavelength converters due to the advantages of high stability, defect-free structure, easy fabrication and high efficiency.¹³ Figure 6.7 shows the device structure of a blue LED pumping yellow phosphors and the corresponding emission spectrum. The yellow phosphor was coated on the LED chip which can be fabricated during the packaging process. Some of the blue emission is absorbed by the phosphor which re-emits the yellow light. Other blue light comes out of the device and white light can be obtained. The blue emission from the LED is relatively narrow, with FWHM of 50 nm.

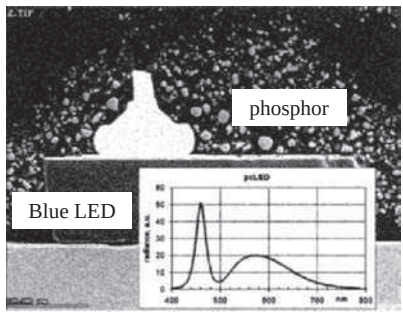


Figure 6.7 White LED structure consisting of yellow phosphor pumped by a blue LED and its emission spectrum.¹³ (Source: Mueller-Mach, R., Mueller, G.O., Krames, M.R. and Trotter, T., High-power phosphor-converted light-emitting diodes based on III-nitrides. *IEEE J. Sel. Top. Quantum Electron.*, **8**, 339. © 2002 IEEE)

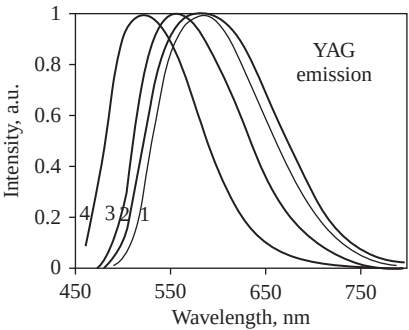


Figure 6.8 Emission spectra of YAG phosphors with different compositions: ‘1 → 3’ with decreasing gadolinium concentrations and ‘4’ with high gallium concentrations.¹³ (Source: Mueller-Mach, R., Mueller, G.O., Krames, M.R. and Trottier, T., High-power phosphor-converted light-emitting diodes based on III-nitrides. *IEEE J. Sel. Top. Quantum Electron.*, **8**, 339. © 2002 IEEE)

In contrast, the phosphor emission is quite broad, which is determined by the material and can be fine tuned.

One of the most successful yellow phosphor materials is yttrium aluminum garnet (YAG) doped with Ce^{3+} ions ($\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$).¹³ As shown in Figure 6.8, with the incorporation of gadolinium and gallium, the emission peak of the phosphor ($\text{Y}_{1-x}\text{Gd}_x$)₃($\text{Al}_{1-y}\text{Ga}_y$)₅ $\text{O}_{12}:\text{Ce}^{3+}$ can be red- and blue-shifted, respectively. The absorption peak of the phosphor is around 460 nm, which is suitable for blue LED pumping. The thickness of the phosphor layer is varied to adjust the relative intensity between blue and yellow emission. Peak wavelengths of these two complementary colors are also close to the upper theoretical limit of white light generation. In this system, the energy loss from the Stokes shift is not so serious since the blue part is directly emitted from the LED, rather than from the phosphor. However, the CRI value is typically less than 80 using this two-color mixing. UV LEDs pumping RGB phosphors can effectively increase the CRI value since the emission characteristic is determined by the broad-band emission from the phosphors. Besides, if a deep-UV LED is used (200 to 320 nm), the mature phosphor technology that is typically used in fluorescent lamps can be applied. However, the large Stokes shift is a problem for this technology.

6.3 Diode characteristics

When a p-layer and an n-layer come into contact, a p–n junction forms and shows diode characteristics, ideally which means the device behaves like a short and open circuit under forward and reverse bias condition, respectively. There are more holes (electrons) than electrons (holes) in the p- (n-) layer. Hence, the holes (electrons) diffuse from p- (n-) to n- (p-) side near the p–n junction and recombine with opposite carriers, as shown in Figure 6.9(a).²⁶ After carrier annihilation, negative and positive space charge is left behind which creates an internal electric field from n- to p-side. This internal field results in the band diagram bending, as shown in Figure 6.9(b). By using the Poisson equation, which is derived from the boundary condition of Maxwell’s equation, one can obtain the relation between the donor and acceptor concentrations and the built-in voltage. This space charge region is nearly free of carriers under thermal equilibrium and is called the ‘depletion region’. Holes and electrons experience the built-in voltage and then drift toward p- and n-side, respectively. Such drift current balances the diffusion current and no net current flows under thermal equilibrium, as shown in Figure 6.9. Under this condition, one can also note the Fermi level of the p- and n-side is aligned due to the band bending. When a forward bias is applied (a voltage from p- to n-side), it cancels the built-in voltage. Once the forward bias exceeds the

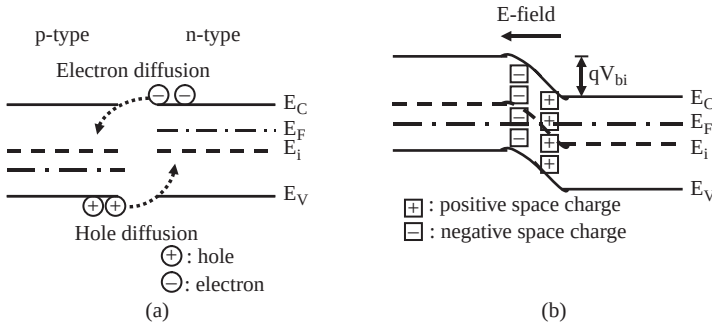


Figure 6.9 Band diagram of a p–n junction (a) before and (b) after contact under thermal equilibrium.

built-in voltage, the current density shows an exponential increase with applied voltage, which is called the threshold voltage. The value of threshold voltage of a LED is approximately E_g volts (which is the bandgap energy in terms of eV) under high carrier concentrations. Layers of p- and n-type here are used to transport carriers into the depletion region for recombination. Hence, the resistance of the p- and n-layer should be as small as possible to reduce the ohmic loss in these regions. Also, this decides the width of the depletion zone, which in turn affects the recombination zone and recombination efficiency. For this kind of homojunction structure, however, there is still some carrier leakage, i.e. holes and electrons propagating to the cathode and anode, respectively, without recombination due to the inefficient carrier confinement. Heterojunction and electron blocking layer are used to prevent carrier leakage to the opposite electrodes. Furthermore, quantum structures (well, wire and dot) are used to confine carriers in a specified recombination region. Energy levels in the quantum structures are discrete, which allows one to fine-tune the emission wavelength, and increase the flexibility during epitaxial growth.

6.3.1 The p-layer and n-layer

A LED is basically formed by a p–n junction. Holes and electrons transport through the p- and n-layers, respectively, and then recombine in the active region. To reduce ohmic loss at the p- and n-layers, the resistance of these materials should be as small as possible, which can be achieved by increasing the carrier concentration (and also the carrier mobility). Carrier concentration in these layers also determines the width of the depletion region, which affects the recombination zone in a homojunction LED. By incorporating group IV (e.g. Ge and Si) and VI (e.g. S, Se and Te) materials into III–V compounds to replace the group III and V atoms, it is possible to achieve n-type doping.¹¹ Figure 6.10(a) shows a schematic of Se doped into GaAs and replacing the As site. Since Se has one more valence electron than As, it ‘donates’ one electron to the crystal. This extra electron can be considered as nearly free, since no bond is formed with the crystal. However, it is still attracted by the positively charged Se atom which is similar to the binding between the electron and nucleus of a hydrogen atom. Hence, one can define a binding energy of the donor (E_D) slightly below the conduction band in the forbidden gap, and treat it as a trap state. Since it is a shallow trap, the thermal energy is enough to excite the electrons to the conduction band as free electrons. Similarly, p-type doping can be achieved by using Cd, Zn, Mg and Be (group II) and C and Si (group IV) atoms to replace the group III and V atoms, respectively. Figure 6.10(b) shows an example of Zn doped in GaAs and replacing the Ga atom. Acceptors create an acceptor energy (E_A) above the valence band within the forbidden gap. Electrons in the valence band can be thermally excited to the acceptor state, which looks like a free ‘hole’ created in the valence band.

Typically, the effective mass of holes is much greater than that of electrons, which results in E_A being greater than E_D . Hence, the thermal energy required for free-hole creation is much larger than for electrons,

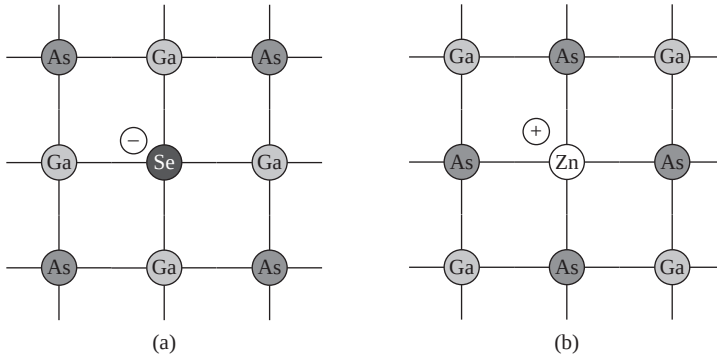


Figure 6.10 Schematic of bonding of GaAs with (a) Se and (b) Zn impurities.

which means the ‘ionization’ of holes is sometimes not complete and limits the p-doping concentration, especially for wide-gap nitride semiconductors. For example, E_A of Mg-doped GaN is 0.2 eV and much higher than the thermal energy (~ 25 meV at room temperature) which means only a small portion of acceptors are ionized and contribute to hole carrier concentrations. Sometimes, the dopant does not exactly replace the original atoms, which results in low carrier concentration. For example, Mg doped in GaN does not occupy the Ga site as grown and leads to a low hole concentration. After low-energy electron beam irradiation (LEEBI), the Mg atoms move to the exact Ga sites and contribute to hole concentration. Unintentional introduction of impurities during epitaxy and processing results in defect trap levels which compensate the doping level; for example, oxygen contamination for aluminum-containing compounds and hydrogen passivation for nitride compounds. A suitable post-annealing process is required to remove these impurities.

Another way to reduce the resistance of the p- and n-layers is to increase the mobility value. Typically, hole mobility in III–V compounds is much less than that of electrons due to their larger effective mass. For example, μ_n and μ_p are 5000 and 300 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ in n- and p-type GaAs with doping concentration of 10^{17}cm^{-3} at room temperature. There exists a tradeoff between the carrier concentration and carrier mobility. With increasing dopant concentration, the impurities scatter the carriers and reduce the carrier mobility. Typically, it is more effective to reduce the resistance by increasing the carrier concentration.

6.3.2 Depletion region

In this section, we quantitatively describe two important parameters of the depletion region, built-in voltage and depletion width. As shown in Figure 6.9, the built-in voltage comes from band bending in the depletion region. In contrast, in the p- and n-layers, the band is still flat. As discussed in Chapter 3, assuming the acceptors and donors are fully ionized, then hole and electron concentrations can be represented as²⁶

$$p = n_i \exp \left[\frac{E_i - E_F}{(kT/q)} \right] = N_A, \quad (6.7)$$

$$n = n_i \exp \left[\frac{E_F - E_i}{(kT/q)} \right] = N_D, \quad (6.8)$$

where p and n are hole and electron concentrations far away from the depletion region, respectively, n_i is the intrinsic concentration and E_i and E_F are the Fermi energies of intrinsic and doped layer in terms of

eV, respectively. Note that although the Fermi level looks flat throughout the whole p–n junction as shown in Figure 6.9, the Fermi energies with respect to the conduction band and valence bands are different in p- and n-layers, far away from the depletion region. K is the Boltzmann constant, T is the temperature and N_A and N_D are the acceptor and donor concentrations, respectively. Hence, one can obtain ψ_p , ψ_n and built-in voltage $V_{bi} = (\psi_n - \psi_p)$ as shown in Figure 6.9:

$$\psi_p = -(E_i - E_F) = -\frac{kT}{q} \ln \left(\frac{N_A}{n_i} \right), \quad (6.9)$$

$$\psi_n = -(E_i - E_F) = \frac{kT}{q} \ln \left(\frac{N_D}{n_i} \right), \quad (6.10)$$

$$V_{bi} = \psi_n - \psi_p = \frac{kT}{q} \ln \left(\frac{N_A N_D}{n_i^2} \right). \quad (6.11)$$

One can note that with increasing doping concentrations, V_{bi} increases. In LED applications, for reducing device resistance and hence less power consumption, heavily pn-doped layers are needed and the Fermi levels of the p- and n-layers are close to the valence and conduction bands, respectively. Hence, one can note that V_{bi} is close to the bandgap of the semiconductor. When the applied voltage is higher than V_{bi} , then the band bends to the reverse side to the equilibrium case. Under this bias condition, holes and electrons transport easily from p- and n-type layers to the opposite side, which results in an exponential increase in current density as described in the next section.

From electromagnetic wave theory, Gauss's law can be represented as

$$\nabla \cdot (\epsilon E) = \rho, \quad (6.12)$$

or can be written as Poisson's equation:

$$\nabla^2 V = -\rho/\epsilon, \quad (6.13)$$

where E is the electric field, ϵ is the electric permittivity, ρ is the charge density and V is the voltage. Assuming the free carriers are fully ionized in the depletion region, then the distributions of space charge, electric field and voltage are as shown in Figure 6.11. The electric field distribution can be obtained from

$$E(x) = \int \rho(x) dx$$

$$\rho(x) = \begin{cases} -qN_A; & -x_p < x < 0 \\ +qN_D; & 0 < x < x_n \end{cases}, \quad (6.14)$$

where x_p and x_n are the boundary of the depletion region at p and n side, respectively. Hence, the maximum electric field (E_{max}), which occurs at the p–n boundary, is given by

$$E_{max} = \frac{q}{\epsilon} N_D x_n = \frac{q}{\epsilon} N_A x_p. \quad (6.15)$$

One has to note that

$$x_n + x_p = W, \quad (6.16)$$

where W is the width of the depletion region. Hence, the depletion region under thermal equilibrium (V_{bi}) can be represented as

$$V_{bi} = \frac{1}{2} E_{max} W \quad (6.17)$$

or

$$W = \sqrt{\frac{2\epsilon}{q} \left(\frac{N_A + N_D}{N_A N_D} \right) V_{bi}}. \quad (6.18)$$

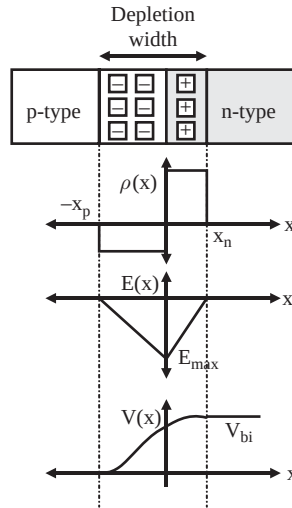


Figure 6.11 Charge density, electric field and voltage distribution of a LED under thermal equilibrium.

when a forward bias V is applied, V_{bi} in Equation (6.18) is replaced by $(V_{bi} - V)$, which results in a reduction in the depletion width. In contrast, the depletion region increases under reverse bias. With a narrower depletion region, it is easier for carriers to transport across through to the opposite site, leading to higher current density. In contrast, the wider depletion region under reverse bias impedes carrier transport, which explains the rectification effect of the p-n diode.

Example 6.2

Consider a GaAs p-n diode at room temperature. The intrinsic carrier concentration n_i is $1.79 \times 10^6 \text{ cm}^{-3}$ and the doping levels are $N_A = 5 \times 10^{19} \text{ cm}^{-3}$ in the p-side and $N_D = 10^{16} \text{ cm}^{-3}$ in the n-side. Find the built-in voltage, depletion width and maximum electric field. (Note that $\epsilon_r = 13.18$ for GaAs.)

Answer. From Equations (6.9) and (6.10),

$$\psi_p = -\frac{kT}{q} \ln \left(\frac{N_A}{n_i} \right) = -\frac{300 \times 1.381 \times 10^{-23}}{1.6 \times 10^{-19}} \ln \left(\frac{5 \times 10^{19}}{1.79 \times 10^6} \right) = -0.8013 \text{ V},$$

$$\psi_n = -\frac{kT}{q} \ln \left(\frac{N_D}{n_i} \right) = -\frac{300 \times 1.381 \times 10^{-23}}{1.6 \times 10^{-19}} \ln \left(\frac{10^{16}}{1.79 \times 10^6} \right) = 0.5808 \text{ V}.$$

The built-in voltage V_{bi} from Equation (6.11) is $V_{bi} = \psi_n - \psi_p = 1.3821 \text{ V}$.

From Equations (6.17) and (6.18),

$$\begin{aligned} W &= \sqrt{\frac{2\epsilon}{q} \left(\frac{N_A + N_D}{N_A N_D} \right) V_{bi}} = \sqrt{\frac{2 \times 13.18 \times 8.85 \times 10^{-14}}{1.6 \times 10^{-19}} \left(\frac{5 \times 10^{19} + 10^{16}}{5 \times 10^{19} \times 10^{16}} \right) \times 1.3821} \\ &\cong 4.48 \times 10^{-5} \text{ cm}, \\ E_{\max} &= \frac{2V_{bi}}{W} \cong 61\,700 \text{ V cm}^{-1} \end{aligned}$$

6.3.3 J - V characteristics

Carrier transport in a semiconductor can be divided into carrier diffusion and drift. Diffusion means carriers diffuse from high to low concentrations. Drift current means carrier transport effected by an electric field. Hence, carrier transport, taking hole current density, J_p , as an example (total current density is the sum of the electron and hole current densities), can be represented as²⁶

$$J_p = J_{p,\text{diff}} + J_{p,\text{drift}}, \quad (6.19)$$

$$J_{p,\text{diff}} = qD_p \frac{dp}{dx}, \quad (6.20)$$

$$J_{p,\text{drift}} = pq\mu_p, \quad (6.21)$$

where $J_{p,\text{diff}}$ and $J_{p,\text{drift}}$ are hole diffusion and drift current density, respectively, D_p is the diffusivity and μ_p is the hole mobility, defined as the velocity (in cm s^{-1}) over the electric field (V cm^{-1}). Under thermal equilibrium, holes and electrons diffuse from p- and n-layers to the opposite side, which is balanced by the drift current from n- to p-side. As shown in Fig. 6.12, since drift current depends on the electric field, there is no drift current outside the depletion region, where the band is flat. When a forward bias is applied, built-in voltage decreases and current density increases. Since the built-in voltage decreases with increasing forward bias, the barrier for carrier diffusion decreases which results in a net current from the p- to n-side under forward bias.

Although there is no explicit form to illustrate the carrier distribution in a LED, which is essential to derive the J - V characteristics, we can still qualitatively describe it as shown in Figure 6.13. Parameters p_{p0} , n_{n0} , p_{n0} and n_{p0} are the hole concentration in p-layer, electron concentration in n-layer, hole concentration in n-layer and electron concentration in p-layer, respectively, before p-n junction formation. One can note that near the depletion boundary, the minority carrier concentrations p_n and n_p are higher than p_{n0} and n_{p0} , respectively, which results in a diffusion current for holes and electrons in n- and p-layers. Typically, the J - V characteristics can be approximately represented as

$$J = q \left[\sqrt{\frac{D_p}{\tau_p}} N_A + \sqrt{\frac{D_n}{\tau_n}} N_D \right] \exp \left[\frac{q(V - V_{bi})}{kT} \right], \quad (6.22)$$

where τ_n and τ_p are the minority carrier lifetimes, respectively. One can note that once the voltage is over V_{bi} (approximately the value of E_g in terms of eV) an exponential increase in current density is observed. This ‘threshold’ voltage is reasonable. Since the LED emits a photon with wavelength $\lambda = hc/E_g$, one has to provide the driving voltage of at least $V = E_g/q$. Hence, it is straightforward that the driving voltage of shorter wavelength (blue LED) is higher than that of longer wavelength (red LED). One of the disadvantages of this structure, which is called a ‘homojunction’ structure, is the carrier leakage problem.

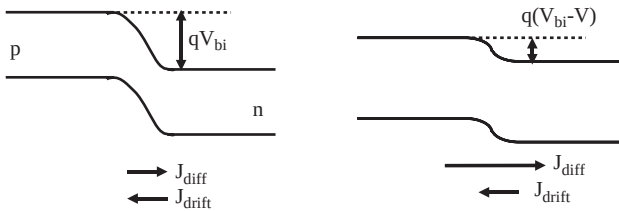


Figure 6.12 Band diagram of a LED under (a) thermal equilibrium and (b) forward bias.

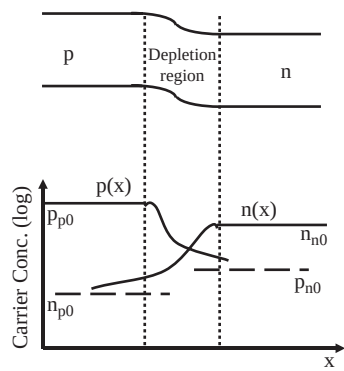


Figure 6.13 Carrier distribution under forward bias.

Since the holes and electrons diffuse into the n- and p-side for recombination, with their carrier lifetimes of τ_p and τ_n , it is possible for carriers to leak to the electrode before recombination if the time constants are long enough, which results in a reduction of the efficiency. Such a drawback can be overcome by careful design of the device structure, as discussed in the following sections.

6.3.4 Heterojunction structures

Since the bandgap of III–V semiconductors can be adjusted by varying their compositions, materials with different bandgaps can be applied to different layers of a single device during the epitaxial growth, which is called a heterojunction structure.²⁷ A LED with single composition (bandgap) described in the previous section is referred to as a ‘homojunction’ device. Heterojunction structures can be used to confine the carriers in the active region to increase the recombination rate. Figure 6.14(a) shows a single-heterojunction (SH) structure. In this type of LED, p- and n-type materials are different. The p-layer exhibits a smaller bandgap than the n-layer. ΔE_c and ΔE_v denote the energy difference of the conduction and valence bands between two materials, respectively. The sum of ΔE_c and ΔE_v represents the bandgap difference between p- and n-type materials. For a hole transporting from p- to n-type material, it encounters an extra barrier height ΔE_v which decreases the hole current into the n-region.

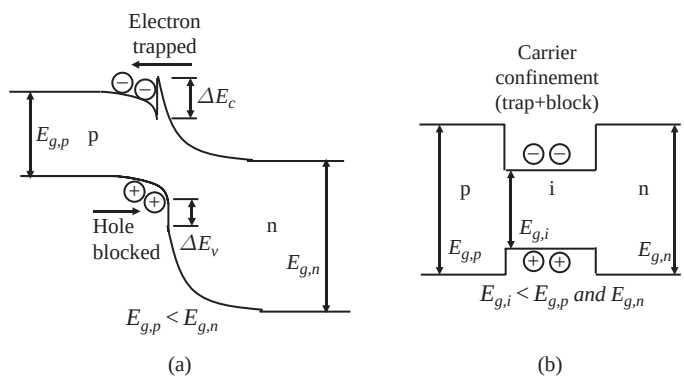


Figure 6.14 Band structures of (a) single- and (b) double-heterojunction LEDs.

On the other hand, the electron is energetically preferred to inject into the p-side, and possibly be trapped in the ‘energy well’ formed by ΔE_c . Hence, many electron–hole pairs accumulate at the p-side near the SH interface which increases the recombination rate and the internal quantum efficiency. Typically, in a heterostructure the small-bandgap material, the p-side in this case, is designed as the emitting layer. In contrast to the homojunction devices, the recombination zone of SH-LEDs is mainly determined by the energy difference and layer structure. Hence, the p- and n-doping concentrations can be optimized without considering the depletion region width which affects the recombination zone of homojunction LEDs, as described in previous sections.

Furthermore, one can apply the heterojunction at both the p- and n-type materials at the same time, which is called a ‘double heterojunction’ (DH) structure, as shown in Figure 6.14(b). An active layer with a smaller bandgap is sandwiched by two wide-bandgap materials (typically called cladding or confinement layer), which ensures the carriers injected into the active layer are confined in this region for a higher recombination rate. Due to the imbalance of carrier mobilities ($\mu_n \gg \mu_p$), electrons penetrate easily into the p-side. Hence, an electron blocking layer (EBL) is inserted between the active layer and p-type region to stop electrons with a large bandgap and ΔE_c , as shown in Figure 6.15.²⁸

6.3.5 Quantum well, quantum wire and quantum dot structures

By inserting a thin layer with a lower bandgap in the active region of a heterostructure, the emission zone can be spatially specified and hence the recombination rate can be further increased, which is proportional to the product of the electron and hole concentrations. Reabsorption probability also decreases since the emission zone is very thin and exhibits a small bandgap. Such a thin layer is typically less than 20 nm, which is so small that the matter wave characteristic of the electron is obvious (Section 3.2.1). That is, the energy level becomes quantized, called a ‘quantum well’ (QW) structure, as shown in Figure 6.16.²⁷ The quantized energy levels can be adjusted by changing the composition and width of the QW, which allows other parameters for fine-tuning the emission wavelength. Another advantage of the QW structure comes from its ultrathin width (compared with the 1 μm thickness of the active layer of the heterostructure) which enables the possibility of lattice mismatch growth to be applied before the strain relaxation. Note that the strain also affects the quantized levels which results in some emission wavelength shift.

A QW structure is an ultrathin layer, with quantized level along the epitaxy direction. The composition in the 2-D plane perpendicular to the epitaxial growth is continuous. As shown in Figure 6.17, when a

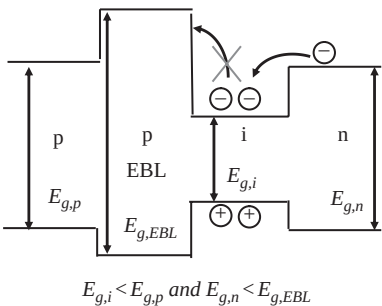


Figure 6.15 Band structures of a LED with EBL.

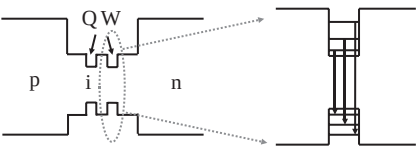


Figure 6.16 Band diagram of a QW structure.

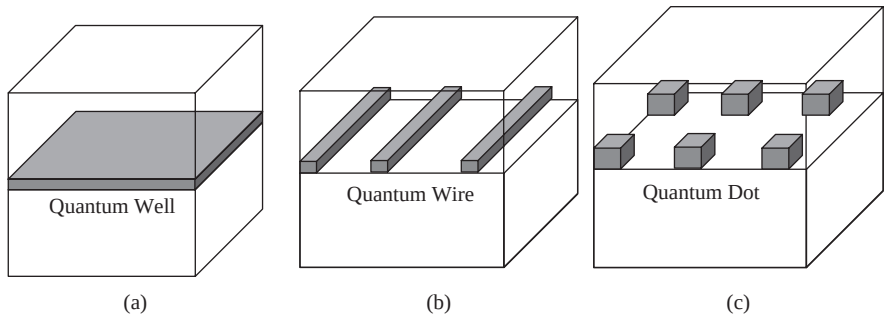


Figure 6.17 Structures of (a) quantum well, (b) quantum wires and (c) quantum dots.

low-bandgap material can be fabricated like wires and dots, then carriers are continuous only in one and zero dimensions, respectively, which are called ‘quantum wire’ and ‘quantum dot’ (QD) structures.²⁹ In contrast to the precise control during epitaxy, fabrication of quantum wires and dots is more difficult since high-resolution pattern definition and epitaxial regrowth are needed. One special case is the nitride semiconductor. Since indium clusters form during epitaxy, which results in some composition fluctuation, some quantum dot structures are grown unintentionally, which also results in a higher recombination efficiency.

6.4 Light-emitting characteristics

Once electron–hole pairs recombine, the energy may relax radiatively or nonradiatively. To decrease the nonradiative rate, one of the most important things is to obtain a high-quality epitaxial layer. Since the bandgap originates from the crystalline structure, defects act as quenchers which results in an efficiency decrease. Such a periodic structure may be destroyed during the fabrication process (e.g. a cleaved facet and etched surface). Some post-annealing processes are needed to reduce the nonradiative recombination rate. Radiative recombination in LEDs is of Langevin type, which is proportional to the product of the electron and hole concentrations. Under some approximations, a linear relation between the injection current and light output can be obtained. The emission spectrum from a LED depends on the density of states and the carrier distributions. Densities of states of the bulk, QW, quantum wire and QD structures are different which results in a shift of the peak wavelength and change of the FWHM. Spectral shift can be observed under different temperature and injection levels. Once the photons are generated, the next step is for them to radiate out of the semiconductor. Due to the large refractive index (typically over 3) of semiconductors, total internal reflection limits the extraction efficiency. Also, for the III–P LEDs, the generated visible photons may be absorbed by the absorbing GaAs substrate.

6.4.1 Recombination model

Radiative recombination in LEDs involves holes and electrons. Once these two opposite carriers meet in the spatial domain, the recombination process happens which is a bimolecular process and can be described in Langevin form:

$$R_{\text{rad}} = r_{\text{rad}}np, \quad (6.23)$$

where R_{rad} is the radiative recombination rate, n and p are electron and hole concentrations, respectively, and r_{rad} is the bimolecular recombination coefficient. When the semiconductor is excited, electrons are promoted from the valence band to the conduction band, which create the same number of holes in the valence band. This means the numbers of ‘excess’ holes and electrons are the same, so

$$\Delta n = \Delta p, \quad (6.24)$$

where Δn and Δp are excess electron and hole concentrations, respectively. For a doped semiconductor, i.e. p-type material, the hole concentration is much higher than the electron concentration under thermal equilibrium, and hence one can obtain

$$p_0 \gg n_0, \quad (6.25)$$

where p_0 and n_0 are the hole and electron concentrations under thermal equilibrium, respectively. Under low-level excitation (excess carriers are much fewer than majority carriers under thermal equilibrium; $\Delta p \ll p_0$), one can write

$$R_{\text{rad}} = r_{\text{rad}}np = r_{\text{rad}}n(p_0 + \Delta p) \approx r_{\text{rad}}np_0 = \frac{n}{\tau_{\text{rad}}} \quad (6.26)$$

and

$$\tau_{\text{rad}} = \frac{1}{r_{\text{rad}}p_0}, \quad (6.27)$$

where τ_{rad} is called the radiative lifetime. We note that the radiative lifetime in doped semiconductors under low-level injection is inversely proportional to the doping concentration. That means recombination is ‘faster’ with higher doping concentrations since there are more majority carriers for participating in the radiative recombination, according to the bimolecular recombination process.

Energy relaxation not by photons but by phonons (lattice vibration) is called nonradiative recombination. In a crystal semiconductor, the main cause for nonradiative recombination arises from the defects of the periodic structure, e.g. lattice structure interrupted at interfaces (surface recombination), dislocations and impurity contamination during ingot growth and epitaxy, and process-induced defects (lattice damage after ion implantation and bombardment, etching of surfaces and cleaving of facets). These defect structures can be quantitatively described by the ‘trap states’ which possibly exist inside the forbidden bandgap. Electrons (holes) jump between the conduction (valence) band and the trap states via phonon and photon intermediation. Although the gap states can help photon emission in some indirect bandgap semiconductors (such as doping nitrogen in GaP), typically they act as luminescence quenchers for most direct bandgap materials.

Quantitative analysis of recombination via traps was accomplished by Shockley and Read³⁰ and Hall.³¹ A schematic illustration is shown in Figure 6.18. Typically, one trap can capture and emit one electron (hole) to and from the conduction (valence) band. Once an electron and a hole are simultaneously captured by a trap before they emit, recombination occurs. When the trap is near the conduction band (i.e. shallow-trap condition), we can imagine that the electrons are easily captured and emitted by the trap, but it is difficult for the holes. Only when the trap is located near the mid-gap (i.e. deep-trap condition) is the recombination rate high. For a doped semiconductor (e.g. p-type material) with deep-trap distribution, although the equation derivation is relative complex, we can still understand that: (1) since there are

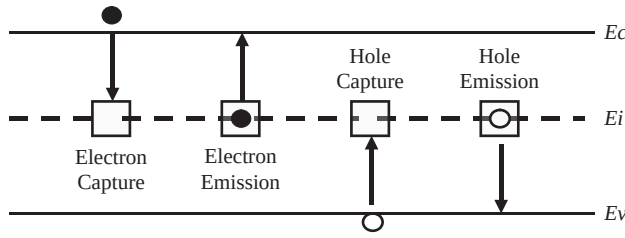


Figure 6.18 Recombination (typically nonradiative) via deep-level traps.

many more holes than electrons, recombination takes place once an electron is captured which means the lifetime of nonradiative recombination is determined by the minority carrier concentration and (2) the traps are typically filled with holes because the traps are distributed near the mid-gap, hence the lifetime is independent of hole (majority carrier) concentration. So, one obtains

$$R_{\text{nonrad}} = \frac{n}{\tau_{\text{nonrad}}}, \quad (6.28)$$

where R_{nonrad} and τ_{nonrad} are the nonradiative recombination rate and the nonradiative lifetime, respectively. So, the total recombination rate can be described as

$$R = R_{\text{rad}} + R_{\text{nonrad}} = \left(\frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nonrad}}} \right) n = \frac{n}{\tau}, \quad (6.29)$$

where τ is called the minority carrier lifetime.

6.4.2 L - J characteristics

Typically, a continuity equation is used to describe the carrier concentration change under electrical and optical excitation. For the electron concentration in a p-type semiconductor under low-level injection, one can write

$$\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_e}{\partial x} + G_0 + G_{\text{ext}} - \frac{n}{\tau}, \quad (6.30)$$

where q is the magnitude of electron charge, G_0 is the generation rate under thermal equilibrium which is equal to the recombination rate under the same condition ($R_0 = n_0/\tau$) and G_{ext} is the excess generation rate by optical excitation. Equation (6.30) can be rewritten as

$$\frac{\partial \Delta n}{\partial t} = \frac{1}{q} \frac{\partial J_e}{\partial x} + G_{\text{ext}} - \frac{\Delta n}{\tau}. \quad (6.31)$$

For a LED with electrical pumping under steady state, one can write

$$0 = \frac{1}{q} \frac{\partial J_e}{\partial x} - \frac{\Delta n}{\tau}. \quad (6.32)$$

The output optical power (P_{out}) from a LED can be represented as

$$\begin{aligned} P_{\text{out}} &= \eta_{\text{ext}} P_{\text{generated}} = \eta_{\text{ext}} h\nu A \int \frac{\Delta n}{\tau_{\text{rad}}} dx = \eta_{\text{ext}} \frac{h\nu A}{q} \int \frac{\tau}{\tau_{\text{rad}}} \frac{\partial J_e}{\partial x} dx \\ &= \eta_{\text{ext}} \frac{h\nu A}{q} \frac{\tau}{\tau_{\text{rad}}} [J_e(\text{in}) - J_e(\text{out})], \end{aligned} \quad (6.33)$$

where η_{ext} is the photon extraction efficiency, $P_{\text{generated}}$ is the power generated inside the LED, $h\nu$ is the photon energy, A is the device cross-sectional area, and $J_e(\text{in})$ and $J_e(\text{out})$ are the electron current supplied in and flowing out of the device, respectively. By using a wide active layer to broaden the recombination region or by designing suitable layer structures (e.g. heterojunction and low-dimensional structures) to confine the carriers, the carrier leakage can be effectively reduced. If the electrons supplied into the devices completely recombine with the same amount of holes, then Equation (6.33) becomes

$$P_{\text{out}} = \eta_{\text{ext}} \frac{h\nu}{q} \frac{\tau}{\tau_{\text{rad}}} I, \quad (6.34)$$

where $I (= JA)$ is the electrical current. One can see that the output optical power is proportional to the supply current. To improve the output optical power, one has to increase the extraction efficiency (higher η_{ext}), use a wide-bandgap material (higher $h\nu$) and reduce the radiative recombination lifetime (smaller τ_{rad}). For a planar LED structure, the extraction efficiency is limited by the total internal reflection between the interface of the semiconductor and the air governed by Snell's law, as shown in Figure 6.19. To improve the efficiency, corrugated structures can be designed to destroy the planar structure for coupling out the waveguiding light inside the device. Die shaping can be helpful to redirect the light out of the LED. Packaged by an epoxy dome and reflector not only protects the device but also increases the extraction efficiency. For III–P material systems, since the GaAs substrate is absorptive, this can be replaced with a transparent substrate, also increasing the light outcoupling. Details of the enhancement of extraction efficiency are discussed in Sections 6.5.3 and 6.5.4.

6.4.3 Spectral characteristics

Emission wavelength of a LED is determined by the product of density of states (DOS) and the number of carriers in a certain energy state. DOS means how many states are available for recombination for a certain energy. As shown in Figure 6.3, the band diagram shows a parabolic shape both for conduction and valence bands. So, DOS increases from zero at the band edge with increasing energy. Carrier distributions can be obtained from the Boltzmann distribution which decreases exponentially with increasing energy. A typical emission wavelength from a LED is shown in Figure 6.20, where the emission peak wavelength is a little shorter than the bandgap wavelength. Also, the emission spectrum is asymmetric. There is no allowable state within the energy bandgap. Hence, the long-wavelength edge is sharp. In contrast, one can see a smooth curve at the short wavelength region which arises from the exponential tail of the carrier distribution.

For QW and QD structures, the energy is quantized and hence the DOS is different from that in a bulk semiconductor. Figure 6.21 shows the DOS at different energy for bulk and quantum structures. For QW and QD structures, the DOS are a step and delta function, respectively, due to the energy confinement by the quantized level, which means the emission spectra of the quantum structures have a narrower FWHM and larger color gamut for display applications.

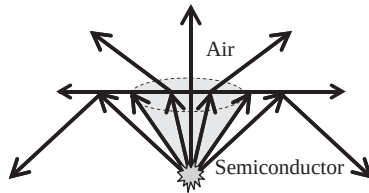


Figure 6.19 Light escape cone of a LED due to the total internal reflection.

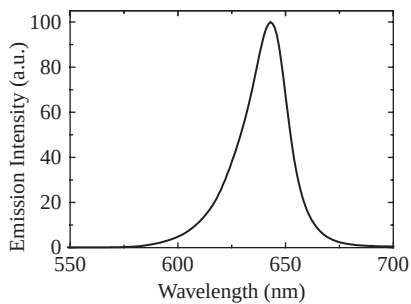


Figure 6.20 Emission spectrum from a LED.

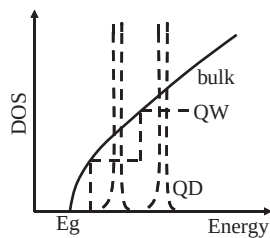


Figure 6.21 DOS of bulk, QW and QD structures.

When increasing the temperature near room temperature, the emission intensity of LEDs decreases and the spectrum red-shifts. Figure 6.22 shows the experimental results of intensity decrease and spectral shift for R, G and B LEDs for different temperatures. The physical mechanism of the intensity decrease mainly comes from the increase of nonradiative recombination. Due to the increase of phonon intensity with increasing ambient temperature, the nonradiative recombination rate increases sharply which, in turn, decreases the intensity. Temperature increase also results in bandgap shift towards lower energy, which results in the spectral red-shifts. These two phenomena are more serious in long-wavelength LEDs, such as shown in Figure 6.22. Such a temperature dependence of a LED results in serious problems for display applications. For example, a LED traffic signal may have different colors and lower intensity at noon than at night, which results in safety issues. For LEDs as LCD backlights, a lot of heat is generated which

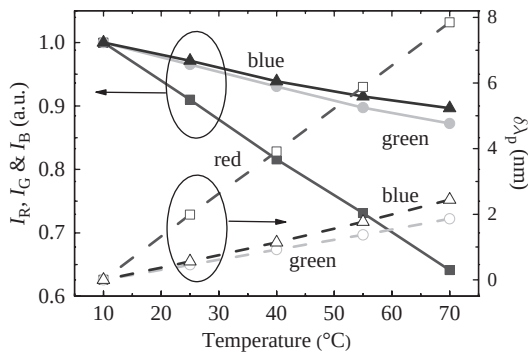


Figure 6.22 Temperature dependence of RGB LEDs.

results in color shift and color gamut change. Hence, suitable temperature control and compensation circuits are needed to optimize the display performances over a wide temperature range.

Example 6.3

White light is generated by red, green and blue LEDs with their primary wavelengths at 650, 550 and 450 nm, respectively, at room temperature (25°C). However, after operating for some time (i.e. 30 min), due to the generated heat, the module temperature increases and stabilizes at 85°C. Assume these three LEDs emit monochromatic light. For the red LED, the peak wavelength red-shifts 5 nm and emission intensity decays 20 % with a 30°C increase in temperature. For the green and blue LEDs, the wavelength shift and intensity decay are 2.5 nm and 5 % per 30°C increase. Find the initial RGB luminance ratio (at 25°C) of a white light source at CIE coordinates of (0.33, 0.33) which stably operates at 85°C.

	Red		Green		Blue	
$\lambda(\text{nm})$	650	660	550	555	450	455
x	0.725	0.730	0.302	0.337	0.157	0.151
y	0.275	0.270	0.692	0.659	0.018	0.023
$V(\lambda)$	0.107	0.032	0.995	1.000	0.038	0.048

Answer. After a long time of operation, the emission wavelength of the red LED shifts and stabilizes at 660 nm:

$$x = \frac{X_r}{X_r + Y_r + Z_r} = 0.73; \quad y = \frac{Y_r}{X_r + Y_r + Z_r} = 0.27; \quad z = \frac{Z_r}{X_r + Y_r + Z_r} = 0 \rightarrow X_r = 2.7Y_r; \quad Z_r = 0.$$

Similarly, we can find the relation between X , Y and Z for the green (555 nm) and blue (455 nm) LEDs: $X_g = 0.5114Y_g$, $Z_g = 0.006Y_g$; $X_b = 6.5652Y_b$, $Z_b = 35.913Y_b$.

The white light consists of RGB LEDs; the X , Y and Z for white light is

$$X_w = X_r + X_g + X_b = 2.7Y_r + 0.5114Y_g + 6.5652Y_b$$

$$Y_w = Y_r + Y_g + Y_b$$

$$Z_w = Z_r + Z_g + Z_b = 0.006Y_g + 35.913Y_b$$

For a white-light source at (0.33, 0.33)

$$\frac{X_w}{X_w + Y_w + Z_w} = 0.33; \quad \frac{Y_w}{X_w + Y_w + Z_w} = 0.33; \quad \text{and} \quad \frac{Z_w}{X_w + Y_w + Z_w} = 1 - 0.33 - 0.33.$$

Hence, one can obtain $Y_r:Y_g:Y_b = 5.02:28.857:1$ at 85°C.

In order to eliminate the thermal effect causing decay of the emission intensity, the initial luminance (25°C) ratio of RGB LEDs would be

$$\frac{Y_r}{(1 - 0.4)} : \frac{Y_g}{(1 - 0.1)} : \frac{Y_b}{(1 - 0.1)} = 7.53 : 28.857 : 1.$$

6.5 Device fabrication

Fabrication of a LED starts from epitaxial growth on a crystalline substrate. There are several epitaxy techniques, such as liquid phase epitaxy (LPE), vapor phase epitaxy (VPE) and metalorganic chemical vapor deposition (MOCVD). LPE is the simplest and most economic technique for obtaining a thick epilayer under thermal dynamic equilibrium conditions, which also limits the semiconductor compositions near the lattice-match condition. The thickness of the epilayer by LPE is controlled by the contact time of the III–V solution and the solid substrate. The fast growth rate results in difficulty in obtaining thin layers, such as QW structures. VPE provides greater flexibility to tune the alloy composition by controlling the gas flow of group III and V materials independently in the vapor phase. Distinguished by their vapor sources, there are chloride, hydride and organometallic VPE methods. Typically, VPE with organometallic sources is typically called MOCVD which is one of the most common ways for obtaining complex layer thicknesses, compositions and doping profiles. Once a high-performance epilayer is obtained, the next step is to fabricate a p–n junction. LED fabrication is relative simple, compared to other III–V devices such as laser diodes and transistors. Suitable electrode materials should be selected and post-annealing may be needed for obtaining an ohmic contact and low serial resistance. Current spreading is used to obtaining uniform emission from the chip. Electrode layout should be well designed since the reflective metal blocks light outcoupling. For improving the extraction efficiency, the epitaxial layer should be well designed to fully open the ‘escape cone’ from the bottom, top and the side walls. Chip shaping and surface engineering are helpful to redirect the light and destroy the waveguiding effects for radiating out from the semiconductor to the epoxy encapsulation layer. The refractive index of the epoxy is as high as possible to increase the critical angle between the semiconductor–epoxy interfaces. And the nonplanar shape of the epoxy is designed to improve the light extraction from the epoxy to the air. Package process is important since it not only protects the LED chips and improves the extraction efficiency, but also improves the thermal dissipation which is an important issue for high-power applications.

6.5.1 Epitaxy

LPE is a useful epitaxial technique for LED mass production, due to its simple process, low cost and high growth rate. A schematic illustration LPE is shown in Figure 6.23.³² Different solutions containing saturated solutions of molten mixtures (e.g. Ga, As, Al) are placed in different source holders (solution bins). GaAs substrate is put on a holder which can contact different melts for obtaining different layer

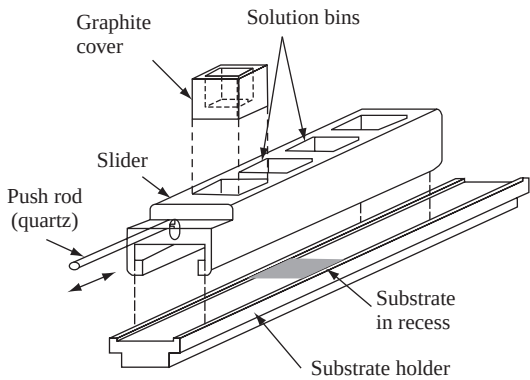


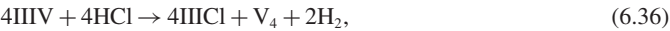
Figure 6.23 Schematic diagram of LPE system.³² (Source: Kupha, E. (1991) Liquid phase epitaxy. *Appl. Phys. A*, **52**, 380 (1991). With kind permission of Springer Science and Business Media)

compositions and doping profiles by moving the push rod. The temperature decreases when the sources and the GaAs substrates contact, and the atoms from the melt in the liquid phase epitaxially grow on the solid substrate under thermal equilibrium condition. The thickness of each epilayer is controlled by the temperature and the contact time. Since the growth temperature is high (about 700 to 900°C), transfer time among different melts should be as short as possible to avoid oxidation reaction occurring which forms defects at the layer interfaces. LPE has a very high growth rate (up to 2 μm min⁻¹) which is suitable for mass production. However, this also causes difficulties in epitaxial growth of thin layers, such as QW structures. Since different atoms (e.g. Al, In, Ga and P) exhibit different distribution coefficients (which is defined as the ratio of concentrations in the solid to the liquid under thermal equilibrium condition), it is difficult to grow AlGaInP layers over GaAs using this technique. It is also difficult to use LPE for III–N systems since nitride is in the gas phase, rather than in the liquid phase. However, LPE works well for the AlGaAs system for red LEDs.

VPE uses gaseous sources, rather than the liquid sources of LPE. Hence, it is easier to control the epitaxial thickness and doping profile, and to grow multilayer structures by adjusting the source gas flow. There are different kinds of VPE systems which can be distinguished by their sources, such as chloride and hydride VPE, and MOCVD, as shown in Table 6.2. Due to the low melting points of the vapor sources, it is possible to achieve ‘vapor phase’ growth even at the temperature range of 600–800°C. Also, it is obvious that some chemical reaction happens due to the use of these vapor sources. Chloride VPE uses solid and gas sources for group III and V, respectively. Group V chloride first reacts with H₂ and forms group V molecules and HCl in the gas phase:



where V means group V materials (e.g. As, P and N). The resulting HCl reacts with the atom or binary compound to obtain the chloride group III sources. In the binary compound case, one can write



where III means group III materials (e.g. In or Ga). Note that this reaction is reversible. When the temperature is high, the reaction tends to shift to the right (which is at the binary compound source region), so the solid sources of group III are etched and form the group III gas sources. Then, at low temperature (where the substrate is placed), the reaction tends to the left forming the epitaxial layer upon the crystalline substrate. Figure 6.24(a) shows a schematic diagram of a chloride VPE system.³³

Note that there are successive reactions in chloride VPE, which means the amounts of group III sources are determined by the group V source. In hydride VPE, the group V sources are replaced by AsH₃ and PH₃, which are then cracked at high temperature to form As₄ and P₄.³⁴ Also, HCl gas is injected to react with group III metal for obtaining the group III gas source:



Table 6.2 Sources used for different VPE systems.

	Group III	Group V	Gas flow
Chloride VPE	Atoms (In, Ga, etc.) or binary sources (GaAs, InP, InAs, etc.)	Chloride (AsCl ₃ , PCl ₃ , etc.)	H ₂
Hydride VPE	Atoms (Ga, In, etc.)	Hydride (AsH ₃ , PH ₃ , NH ₃ , etc.)	HCl and H ₂
MOCVD	Organometallic materials (TMGa, TMAI, TMIn, etc.)	Hydride (AsH ₃ , PH ₃ , NH ₃ , etc.)	H ₂ , N ₂

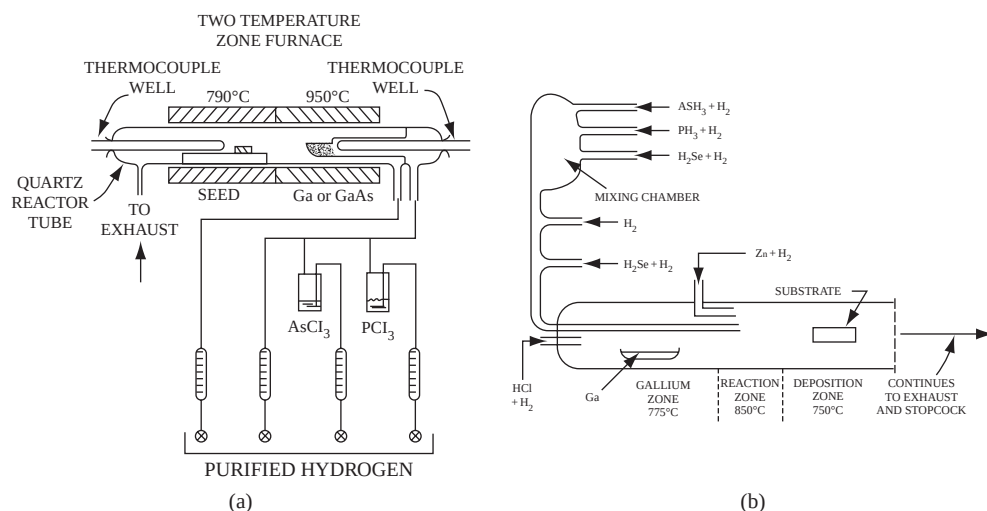


Figure 6.24 Schematic diagram of (a) chloride³³ (reproduced from: Finch, W.F. *et al.* (1964) *J. Electrochem. Soc.*, **111**, 814) and (b) hydride (reproduced from: Tietjen, J.J. *et al.* (1966) *J. Electrochem. Soc.*, **113**, 724) VPE systems.³⁴

Hence, hydride VPE (shown in Figure 6.24(b)) can independently control the amount of group III and V sources and is more flexible for epitaxial growth compared with chloride VPE. Deposition reaction for hydride VPE is the same as for chloride VPE. One of the disadvantages of hydride VPE is the use of the toxic sources of arsine (AsH₃) and phosphine (PH₃).

By using metal alkyls which are liquid or waxy solids at room temperature, the melting points of the group III sources can be greatly reduced. The epitaxial growth technique with metal alkyls and hydrides for group III and V, respectively, is called MOCVD, or organometallic VPE (OMVPE), as shown in Figure 6.25. By using the carrier gas, such as H₂ and N₂, to pass through the group III alkyls and bring the vapor into the growth chamber, the flow rate of group III sources can be controlled precisely. Typical group III sources are: trimethylaluminum, Al(CH₃)₃ (TMAI); trimethylgallium, Ga(CH₃)₃ (TMGa); and trimethylindium, In(CH₃)₃. The MOCVD reaction can be represented as



where V means group V materials (e.g. As, P and N). Note that the reaction is irreversible which means MOCVD is a kind of nonequilibrium growth. The advantages of this growth technique include: (1) possibility for abrupt junctions and thin epilayers and (2) large flexibility in varying the compound

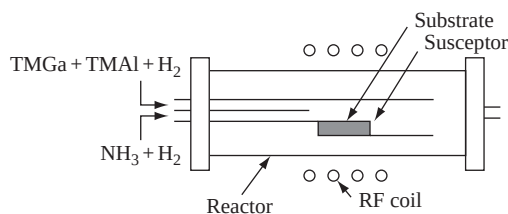


Figure 6.25 Schematic diagram of a MOCVD system.³⁵ (Source: Hirose, K., Hiramatsu, K., Sawaki, N. and Akasaki, I. (1993) Growth of single crystal Al_xGa_{1-x}N films on Si substrates by metalorganic vapor phase epitaxy. *Jpn. J. Appl. Phys.*, **32**, L1039. Reproduced by permission of the Institute of Pure and Applied Physics)

composition. These features are very important in LED applications when quantum structures are applied and different emission wavelengths are required.³⁵ The precise rate control implies a low growth rate ($0.1\text{--}10\text{ }\mu\text{m h}^{-1}$) and can be viewed as a disadvantage of MOCVD.

6.5.2 Process flow and device structure design

Figures 6.26(a) and (b) show typical device structures of III–P and III–N LEDs, respectively. Carriers inject into the LED from the electrode to the p- and n-layers, and then recombine in the active region. Photons are generated and radiate out of the LED structures from the top and both sides for III–P and III–N LEDs, respectively. There are several requirements for the electrode design. First of all, good ohmic contacts between the electrodes and p- and n-layers are needed for good carrier injection. Suitable metal materials and annealing processes can increase the conductivity and reduce the power consumption. Then, the current should pass uniformly through the active layer, which means the resistance of the p- and n-layers should be as small as possible. However, this is not always the case, especially for the wide-bandgap p-type doping. By suitably designing the layout of the electrodes, the carriers can distribute uniformly which results in a dramatic increase in luminous efficiency. A concern for the layout design of the electrodes is that the area of the metal electrode should be as small as possible since it impedes light extraction. Due to the use of insulating sapphire substrate, electrodes of nitride LEDs are fabricated on one side of the substrate, which means mesa etching is required. Nitride semiconductors are rigid which means a strong solution for wet etching or reactive ion etching technique are needed for this step. Then, the LED substrate is diced into individual chips for the package process, which is discussed in Section 6.5.4. Prior to the dicing process, sometimes a wafer thinning process is used to improve the production yield.

Theoretically, direct contact of a metal and semiconductor results in a Schottky diode, rather than an ohmic contact. The barrier height between the metal work function and the carrier transport band (conduction and valence bands for electron and hole, respectively) limits the current injected into the LED. By mixing dopant metal into the electrode sources and annealing the sample, the dopant metal is driven into the semiconductor and reacts with the cladding layer to form a thin heavily doped layer. Hence, an ohmic contact between electrode and semiconductor can be achieved.¹⁴ For AlInGaP and AlGaAs systems, Au–Ge and Au–Zn (or Au–Be) alloys are typically used for the n- and p-type electrodes with dopant concentrations (Ge, Zn, Be) of about 1–15 %, respectively. For p-type contacts, heavy

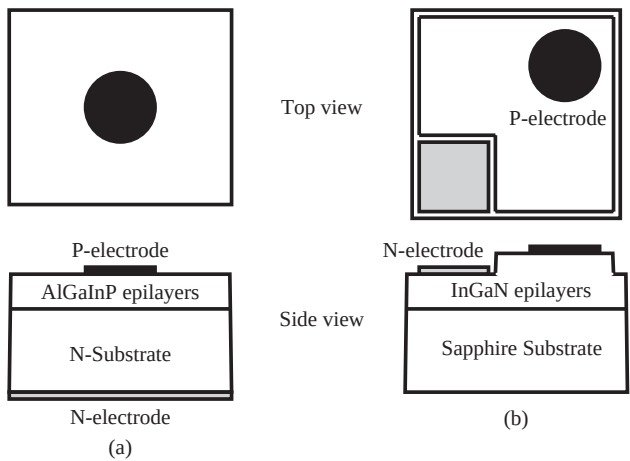


Figure 6.26 Device structures of (a) III–P and (b) III–N LEDs.³⁶

doping can be applied during epitaxial growth (e.g. p^+ -GaAs, p^+ -GaP and p^+ -AlGaAs) to improve the conductivity. However, for the nitride LEDs, heavily doped layers are difficult to achieve. Hence, another approach is to reduce the barrier height of the Schottky junction by using a metal with suitable work function. Ti/Al bilayer and Ni/Au are typical metals used for n- and p-type metallization, respectively. Ti reacts with nitride and forms TiN which is conductive. Ni and Au exhibit high work functions which reduce the barrier between the electrode and the semiconductor.

Typically, the dimensions of LED chips are much larger than the thickness of the p-cladding layer. Hence, holes inject from the anode and recombine with electrons mostly under the opaque metal region, which results in low efficiency. Also, since the recombination rate is proportional to the product of electron and hole concentrations, the nonuniformity of hole distribution results in lower recombination efficiency. One simple method is to increase the thickness of the p-cladding layer, to improve the 'lateral' current flow. This thick layer also serves as the window layer for high extraction efficiency, which is discussed in the next section. Although this technique works well with the AlGaAs system, the high resistance of p-type doping of wider bandgap materials (e.g. AlInGaP and III-N systems) results in higher serial resistance with increasing layer thickness. Another possible solution is to pattern the electrode. By using some 'finger' structures to assist the current spreading, the carrier distribution uniformity can be much improved. However, the area occupied by the opaque electrode should be as small as possible since the metal impedes light extraction. For nitride LEDs, since an insulating substrate is used, the anode and the cathode are on the same side of the substrate, which results in even worse current nonuniformity. Hence, both the p- and n-electrode layout should be taken into consideration. Transparent or semitransparent electrodes such as ITO and thin metals (e.g. Ni/Au or Pt) can be used on the whole area of the devices to improve the current spreading in the p-type region. On the other hand, for III-P LEDs, the ITO can form an ohmic contact only with GaAs cladding layer. Since it is absorptive within the visible region, the GaAs layer should be as thin as possible to reduce the absorption loss.

6.5.3 Extraction efficiency improvement

As mentioned in Section 6.4.2, the extraction efficiency of LEDs is limited by the internal reflection when the light radiates out of the semiconductor planar structure. To improve this, there are typically two methods used: (1) redirecting the light by shaping the whole device and (2) using a nonplanar structure to couple out the waveguiding modes. Combining with the package process (discussed in Section 6.5.4) which increases the critical angle and redirects the light, the extraction efficiency can be effectively increased. Besides, for III-P devices, the photons will be absorbed by the GaAs substrate. It is possible to use a distributed Bragg reflector (DBR) structure between the substrate and the epilayer to prevent light absorption by the substrate, which can act as wavelength selector at the same time. However, this alternative structure increases the complexity and cost in epitaxial growth. There are also some methods to fabricate transparent substrates, instead of absorbing ones. Another issue arises from the metal electrodes which may impede light output. Suitable layout design and device structure are needed to obtain a high extraction efficiency.

From Snell's law, one can obtain the critical angle ($\theta \approx 25.38^\circ$) between the semiconductor (typically $n_{\text{semi}} \approx 3.5$) and the outside medium (typically epoxy in package process, $n_{\text{epo}} \approx 1.5$) and hence define the 'escape cone' shown in Figure 6.19. Assuming the LED is a perfect rectangular solid and light emission is purely isotropic, the six full escape cones are the maximum attainable light extraction. For the absorbing substrate case, obviously the downward escape cone does not exist. Physical dimensions of LEDs are around several hundred micrometers in width and length. The thickness of the active layer is around 1 μm . If the thicknesses of the layers on both sides of the active layer (typically called the cladding layers) are not thick enough ($> 30 \mu\text{m}$) or they are not transparent, the four side cones will be truncated. However, to grow such thick epilayers needs a long time which is not feasible when using the MOCVD technique with a growth rate of $\sim 1 \mu\text{m h}^{-1}$.

For the GaAs/AlGaAs system, the thick cladding layer of large bandgap can be grown by LPE or VPE techniques. By growing a AlGaAs layer of hundreds of micrometers between the active layer and the absorbing substrate, then removing the original GaAs substrate by etching process, a transparent substrate of AlGaAs can be obtained. For the III–P/GaAs system, an upper cladding layer and substrate of transparent GaP is typically used, although there is still a 3.6 % lattice mismatch to the GaAs. By using MOCVD, GaP cladding can be only as high as 15 μm which is not sufficient to open the complete side cones. However, following the MOCVD growth of the active layer, VPE growth of an upper cladding layer of 50 μm has been demonstrated. GaAs substrate can also be removed by etching process, then bonded to the GaP substrate under high-temperature annealing.³⁷ The resulting device structure is shown in Figure 6.27. A transparent substrate is an intrinsic property for the III–nitride devices. However, due to the difficulties in doping, it is not easy to have a thick cladding layer. Besides, a thick cladding may not be very helpful in extraction efficiency because of the high internal absorption loss in the active layer. The light is absorbed by the active layer before it propagates to the edge. Hence, no thick cladding layer is needed. However, as said before, due to the poor conductivity (especially for p-doping), a metal ‘mesh’ electrode is typically used to improve the luminance uniformity which impedes light emission. Hence, a flip-chip structure can be used, as shown in Figure 6.28.³⁸ With the upside-down structure which emits the light from the transparent sapphire, good conductivity and high extraction efficiency can be obtained simultaneously.

The discussions above relate to extracting as much light as possible from a rectangular cubic shape. Actually, it is found that the side cones can extract more light than expected which arises from the nonperfectly planar structure at the edge sides. Besides, the shape of the die can further improve the extraction efficiency by redirecting light to the top-side emission. For example, a trapezoid-shaped structure can effectively reflect the sidewall emission to the top which increases the extraction efficiency. Figure 6.29 shows the evolution of the improvement of light extraction efficiency from a conventional absorbing substrate, a transparent substrate, a ‘finger’ electrode and trapezoid die structures.

Much effort has been made to eliminate the total internal reflection condition in the top side of LEDs. A straightforward method is to roughen the top surface which results in light scattering, rather than reflection. Some periodic nanostructures, such as surface plasmonic coupling and photonic structures, are proven which can effectively diffract out the waveguiding mode. However, there are still some techniques issues in terms of fabrication process, cost and device layout.

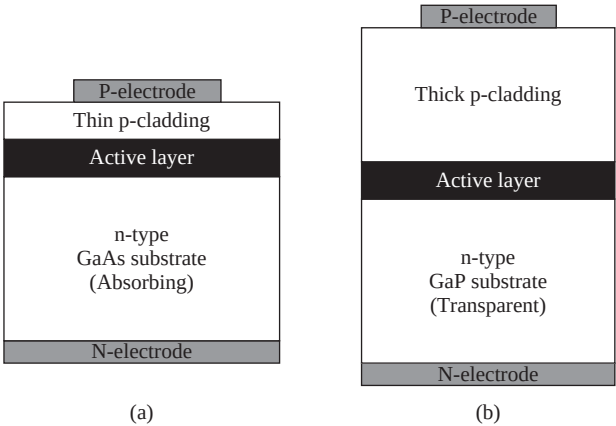


Figure 6.27 (a) Absorbing substrate with thin cladding layer which has one full (upward) plus four partial (sidewall) escape cones, and (b) transparent substrate with thick cladding layer which has six large escape cones.

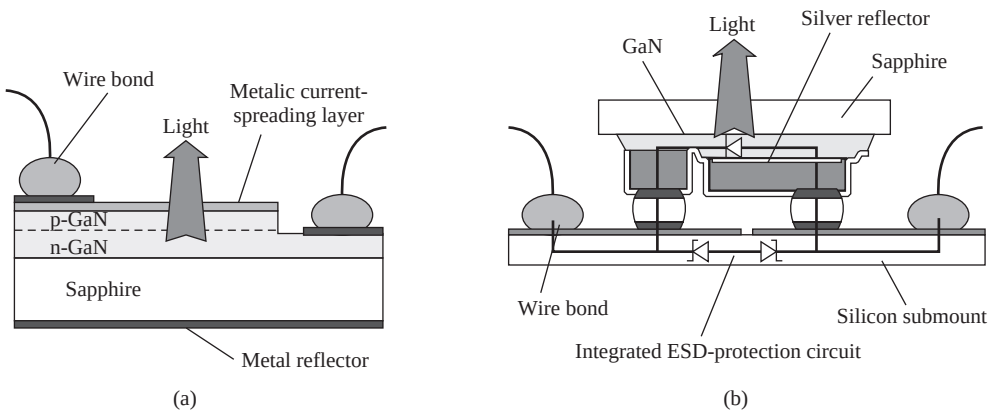


Figure 6.28 (a) Mesh electrode (metallic current spreading layer) and (b) flip-chip III-nitride LEDs.³⁸ (Source: Steigerwald, D.A., Bhat, J.C., Collins, D. *et al.*, Illumination with solid state lighting technology. *IEEE J. Sel. Top. Quantum Electron.*, **8**, 310. © 2002 IEEE)

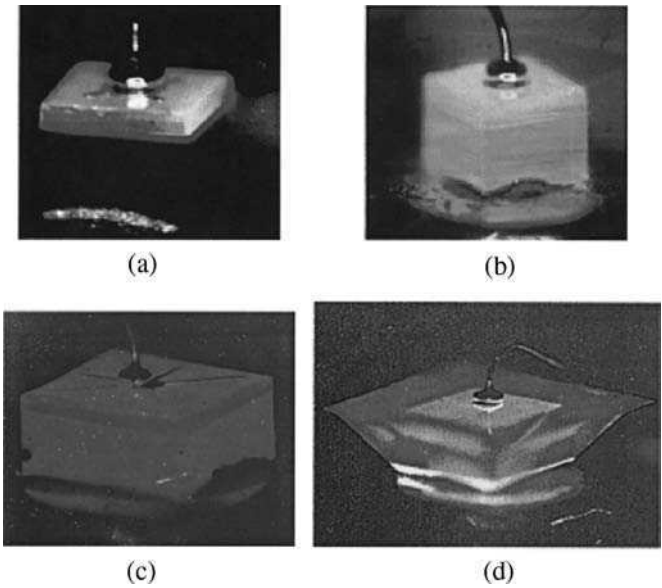


Figure 6.29 Images of LEDs under operation with different geometries: (a) absorbing substrate, (b) transparent substrate, (c) finger electrode arrangement and (d) die shaping structure.³⁸ (Source: Steigerwald, D.A., Bhat, J.C., Collins, D. *et al.*, Illumination with solid state lighting technology. *IEEE J. Sel. Top. Quantum Electron.*, **8**, 310. © 2002 IEEE)

6.5.4 Package

The package process involved in typical semiconductor fabrication has the functions of: (1) protecting the LED and electrode from mechanical and environmental attacks, (2) improving the optical extraction efficiency and (3) helping to dissipate the heat which is especially important for high-power applications. Figure 6.30 shows a packaged LED, a semiconductor chip with dimensions of several hundreds of micrometers mounted on a reflector cup, which redirects the light to the top. Bonding wire is used to

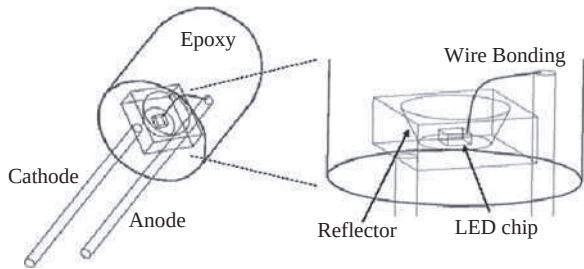


Figure 6.30 Schematic of a packaged LED.

connect the semiconductor and the external electrodes for providing the electrical current. Here, a LED with semiconducting substrate (e.g. AlGaInP on GaAs substrate) is used as an example. Epoxy seals the semiconductor, reflector and bonding wire inside for protection. The shape of the epoxy is typically designed as a hemisphere for enhancing the extraction efficiency at the epoxy–air interface. At the same time, for improving the light extraction at the semiconductor–epoxy interface, the refractive index of epoxy should be as high as possible with low absorption within the visible range to enlarge the escape cone. Typical values of the refractive index of epoxy are around 1.5 to 1.8.

To increase LED optical power, more current should be injected into the device; however, this increases temperature, and, in turn, decreases the optical intensity and red-shifts the emission wavelength. Hence, for high-power LED applications, thermal resistance has to be taken into consideration in designing the package.³⁸ Typically, the LED chip is directly mounted on a heatsink which dissipates the heat from the ‘bottom’ side. Also, silicone rather than epoxy is often used due to its better thermal stability.

6.6 Applications

In earlier years (1960s to 1980s), the applications of LEDs were limited to indicators, alphanumeric displays and simple dot matrix displays for consumer products or industrial use. Also, the colors of LEDs were limited to the long wavelengths of the visible range (such as red) due to the lack of suitable semiconductor materials. Recently, because of the fast developments in epitaxial growth of semiconductor materials and device efficiency improvements, high-performances LEDs have become available which can be used for many different applications. For direct-view applications, LEDs can be used for traffic lights, electronic signage and very large displays. The main concerns for the direct-view displays are the high efficiency (for low power consumption) and correct CIE coordinates. Also, LEDs can be used as the backlight of LCD displays, due to the advantages of their being mercury free, of high color gamut and having a long lifetime and fast response, compared with conventional CCFL backlights. For small LCD displays (such as mobile phones), color gamut is not a main issue. Hence, a white LED (blue + phosphors) can be enough as the backlight source to reduce the cost and minimize the module size. For medium- or large-size LCDs, multicolor LEDs are needed to increase the power efficiency and color gamut. For these applications, the FWHM of the LEDs should be as small as possible to increase the color gamut value. Optical characteristics of LEDs change (intensity and spectrum) due to the ambient temperature and operation time, which are also important for the display qualities. The third category of LED application is general lighting, which can be considered as the light source of reflective displays. For this application, not only should the CIE coordinates of the white LEDs be considered, but a high CRI value is also important which provides objects with a similar look under LED and natural light. However, as discussed in Section 6.2.3, there is a tradeoff between the power efficiency and CRI value.

6.6.1 Traffic signals, electronic signage and huge displays

Definition of colors, luminous intensity and luminance of traffic signals are important in safety issues. Different countries (e.g. the USA, Europe and Japan) have similar but different standards. For example, in the USA, the specifications of traffic signals are regulated by the Institute of Transportation Engineers (ITE), which defines the acceptable color ranges of five distinct colors for traffic signal lighting: red, yellow, blue-green, Portland orange and lunar white. The first three are used for the standard red, yellow and green lights, which mean 'stop', 'caution' and 'go'. The last two colors are used for pedestrian control signals, which are 'don't walk' and 'walk', respectively.

Using LEDs as traffic signals to replace conventional filtered incandescent lamp has two obvious advantages: lower power consumption and longer lifetime. The power efficiency of a typical incandescent source is about 14 lm W^{-1} . To obtain a red traffic light, the green and blue portions are filtered out which results in a power efficiency of $3\text{--}5 \text{ lm W}^{-1}$. For the AlInGaP red LEDs, the power efficiency can be as high as 30 lm W^{-1} , which means a tenfold reduction in power consumption. Compared to the 2- to 3-year lifetime of incandescent lamps, the 10-year operation lifetime of LEDs can further save on maintenance fees. The basic structure of a filtered incandescent lamp is a bulb with a color filter. In contrast, LED traffic signals consist of hundreds of LED pixels (~ 200 to 700 pixels). Failure of one or several LEDs would not affect much the functionality of the traffic signal. Once the bulb is burned out, the incandescent traffic signal fails and replacement is needed. Although the unit 'luminous' price of LEDs is higher than that of the incandescent lamps, the energy and maintenance savings result in total cost savings by using LED technology as traffic signals. LEDs with AlGaInP are typically used for red, orange and yellow traffic lights. InGaN LEDs are used for green and white (blue or UV + phosphor) traffic lights.

There are two disadvantages of LED traffic signals are: (1) the light output variation at different ambient temperatures and (2) the driving circuit complexity. As mentioned in Section 6.4.4, the output intensity decreases and spectrum red-shifts with increasing temperature. Over the range of typical ambient temperature (-40 to 55°C), the CIE shift is not obvious, which will not exceed the range with proper device design. In contrast, the output intensity variation is obvious, which can be compensated by suitable circuit design. Typically, an incandescent lamp is driven by 120 V AC power provided by a traffic signal controller. To use the same controller, an AC-DC converter is needed and a string of LEDs are series connected. A voltage regulator, limiting resistor or constant current sources are needed to provide a uniform light output. To provide some redundancy, which means the random failure of a LED pixel would not affect the functionality of the traffic signal, some parallel connections between different series string are also needed.

Electronic signage and huge displays are other two important applications for LEDs. Due to the fast improvement in LED technology, the colors of electronic signage have improved from monochromatic (typically red), to multiple colors (red, yellow and green) and then to full color (red, green and blue). Compared with conventional electronic signal technologies using small filtered incandescent bulbs, LEDs exhibit the advantages of low power consumption and long lifetime. Also, the resolution can be higher using LEDs due to the small module size. Since the LED can be well passivated by the package process, another advantage is the ruggedness, without the glass envelopes and filaments associated with conventional bulbs. Huge display applications consist of millions of pixels. There are three or four LEDs (red, green and blue) in one single pixel. To achieve maximum white light efficiency, sometimes two red LEDs are needed in one single pixel. Due to the high brightness of the LEDs, huge displays can be viewed even in sunlight.

6.6.2 LCD backlight

Using LEDs to replace conventional CCFLs as the backlight of LCDs has several obvious advantages of low power consumption, long lifetime, small size and ruggedness, as described above. Compared to the several hundred to thousand volts driving CCFLs, LEDs have a much lower driving voltage

(<5 V) which is more suitable for mobile, monitor and TV applications in driving-circuit design and safety issues. Due to the fast response of LEDs, it is very easy to switch the LED backlights on and off to insert the ‘black frames’ to eliminate motion blur behaviors in the hold-type CCFL-LCD due to its impulse-type characteristics. Also, one of the important advantages for LEDs compared to CCFLs is that they are mercury free and environmentally friendly. However, optical requirements of LEDs for LCD backlights is not only the correct CIE coordinates (like the direct-view application described in the previous section), but also: (1) a suitable and narrow emission spectrum to fit the liquid crystal and color filter and (2) luminance uniformity over the whole panel. Figure 6.31 shows the emission spectra of a CCFL and RGB LED, and the transmittance spectra of RGB color filters. The emission spectrum of the CCFL has multiple peaks, although the sharp peaks at 434, 542 and 610 nm correspond to red, green and blue colors, respectively. The peaks at 486 and 585 nm near the overlap of blue–green and green–red color filters result in a decrease of color saturation. Typically, a CCFL LCD has a color gamut of 72 % NTSC. To enlarge the color gamut, one has to decrease the FWHM of the transmission spectra of the color filter. This requires thicker color filter films which results in a decrease in transmission and hence lower efficiency. In contrast, a RGB LED consists of a three-color light source with their FWHMs (typically <50 nm) even smaller than the color filters which results in a high color saturation (105 % NTSC).³⁹

Different from CCFLs, red, green and blue LEDs can be driven individually which makes it possible to light different colors in series to achieve a filter-less LCD. This is called the color sequential or field sequential technique, as shown in Figure 6.32.⁴⁰ In this example, the pixel was intended to display a yellow color, which is a mixture of red and green subpixels. In a conventional CCFL backlight LCD, the liquid crystal lets the red and green subpixel light pass through and blocks the blue light. After the color filter, one can see the yellow color due to the simultaneously lit red and green subpixels. On the other hand, in color sequential driving, blue, green and red LEDs are lit on one-by-one at different time frames. Hence, no subpixel is needed. In this case, the liquid crystal switch is closed only when the blue light is turned on, which makes the red and green rays pass though. Displayed colors come from the color mixtures of LEDs, rather than the color filters. So the color filter is not needed in this scheme. Without the color filter, the fabrication process is simpler and panel cost is reduced. Also, since the color filter absorbs two-thirds and allows only one-third of the light passing through, the color sequential technique can effectively decrease the power consumption. However, since different colors are lit on in series, then the response of liquid crystal materials must be fast enough. Typically, the methods discussed above are suitable for medium and large LCDs, such as for monitor and TV applications. For some small-size LCDs (especially for mobile use), module size is more important than color performances and hence LEDs with phosphor technology will be applied.

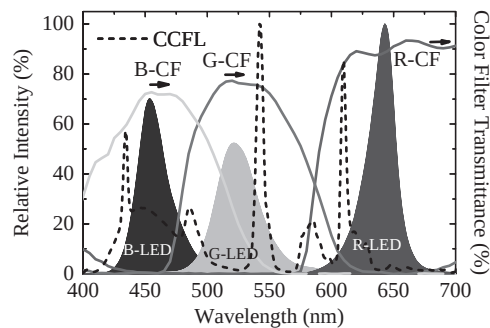


Figure 6.31 Emission spectra of CCFL and RGB LED, and transmittance spectra of RGB color filters.

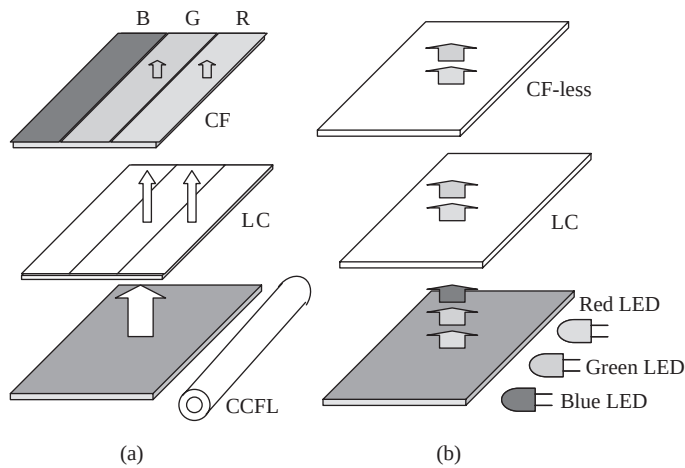


Figure 6.32 (a) Conventional driving and (b) color sequential technique.

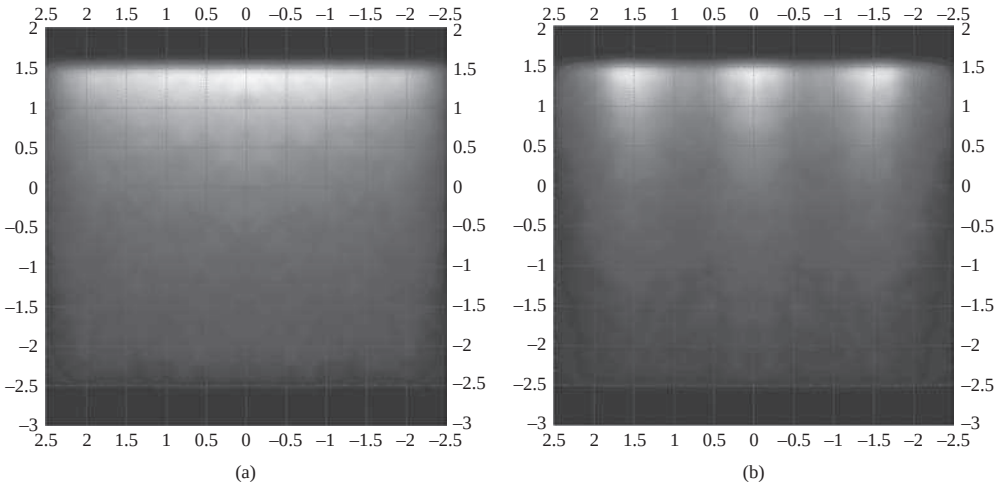


Figure 6.33 Simulation results of luminance distributions of (a) CCFL and (b) LED backlights.

However, since a LED is a point-type light source, optical design is more complex than for a CCFL for obtaining a uniform luminance over a panel. Figure 6.33 shows the simulation results of luminance distributions of the backlight from a conventional linear-type CCFL and a point-type LED. The light source is hidden in the edge of the top side. For the CCFL, the luminance decreases gradually from the top to the bottom sides. On the other hand, obvious high luminance spots can be observed from the LED chips, which results in a serious nonuniformity. Such a phenomenon is even more serious for the 'direct' backlight module, which is an essential technique for large LCDs.

Figure 6.34 shows an example of a LED direct backlight module which uses a printed dot pattern to prevent the bright spots directly emitting from the LEDs. Also, the epoxy dome is carefully designed to couple the light through the light guide and diffuser, rather than emitting towards the liquid crystal layer. After these optical designs, a uniform luminance distribution from LED backlight system can be

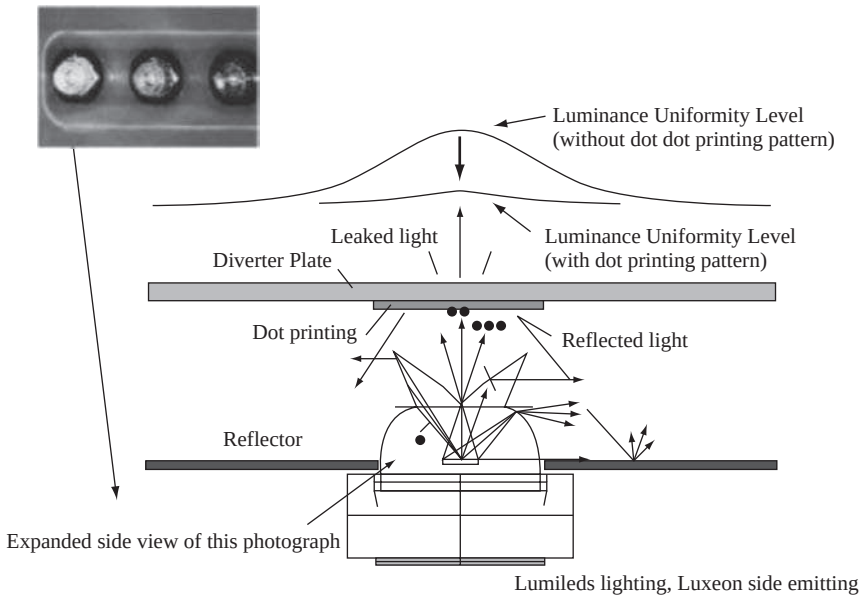


Figure 6.34 LED backlight modules.³⁹ (Source: Kakinuma, K. (2006) Technology of wide color gamut backlight with light-emitting diode for liquid crystal display television. *Jpn. J. Appl. Phys.*, **45**, 4330. Reproduced by permission of the Institute of Pure and Applied Physics)

obtained. Also, the thermal stability and operation lifetime problems should be taken into consideration. LCD temperature increases during operation which results in luminance decay and wavelength red-shifts. Since the operation lifetimes of RGB LEDs are different, differential aging also results in luminance decay, color shift and panel nonuniformity. Some detectors can be implemented on the panel to compensate the brightness loss and correct the color performances.

6.6.3 General lighting

The requirements for general lighting include high power efficiency and high CRI. Hence, a light source with broad-band spectrum is needed. Artificial light sources began with fire, including torches, candles and gas lighting. However, the efficiency is low ($<1 \text{ lm W}^{-1}$) which can be understood from the large heat dissipation accompanying the light emission, which explains why people feel warm under this kind of yellowish bright environment. Typically, this lighting technology involves transfer from chemical to optical energy. Incandescent bulbs and fluorescent lamps are two common lighting sources using electrical input. The input of the bulb is electric power which heats up a tungsten filament in a vacuum without burning it as a torch or a candle. The temperature of the tungsten (about 2856 K) wire determines its color due to its blackbody radiator characteristics (so it is a broad-band source with very good CRI). Actually, the peak wavelength of the bulb is in the infrared rather than the visible region, which results in the low efficiency (so it is hot) and yellowish color (so it is a ‘warm’ light) due to lower color temperature. The lifetime of a bulb is typically several thousands of hours. During operation, the tungsten will be evaporated by the high temperature to the inner side of the glass and the tungsten wire becomes thinner and thinner, and then burns down. Lower temperature results in longer lifetime. However, it shifts the emission peak to longer wavelength and results in lower power efficiency, typically less than 15 lm W^{-1} .

The operation principle of fluorescent lamps is based on the energy relaxation during gas discharge under low pressure. UV emission of the gas (e.g. mercury vapor) from the excited state to the ground state pumps the phosphors to generate visible light. The efficiency of the fluorescent lamp can be several times higher than that of an incandescent lamp, which can be observed in that the temperature of the fluorescent tube is much lower than the bulb. The lifetime of a fluorescent lamp can be as high as several tens of thousands of hours. However, due to the sharp characteristics peaks, the CRI value of a fluorescent lamp ranges typically from 50 to 80.

Because of the fast development in the efficiency of LEDs, they are becoming a promising technology for general lighting applications. For obtaining a good CRI, blue and UV nitride LEDs with phosphors are typically used to broaden the spectrum. Multi-LEDs can be used for higher efficiency. However, since the FWHM from a single LED is about 50 nm, more than three LEDs or suitable layer structure may be needed to broaden the spectrum. Long lifetime (predicted >100 000 hours) and good resistance to the environment are two obvious advantages of LED lighting, compared with bulbs and fluorescent tubes, as discussed in Section 6.6.1. Also, LED lighting has the advantage of being environmentally friendly. Compared with incandescent bulbs, LEDs have a much higher efficiency which results in lower power consumption. Hence, less electric power is needed and carbon oxide emission is reduced. Power saving for the lighting industry is very important since a quarter of all electrical power is used for lighting purposes (including domestic, industry and outdoors). Although the efficiency of fluorescent lamps is comparable to (or slightly less than) that of LEDs, the mercury vapor (used in fluorescent lamps) results in serious environmental problems.

Homework problems

6.1 Derive the following equation:

$$C_{dep} \equiv \frac{dQ}{dV} = \frac{\epsilon}{W}$$

Here, C_{dep} is the capacitance per unit area of depletion region. Q and V are charge per unit area and voltage, respectively. Assume the electric field change (dE) is uniform within depletion region.

6.2 A p-type semiconductor is uniformly photo-excited at $t < 0$. Then, the excitation is turned off at $t = 0^+$, please find the time-dependent minority carrier concentration $n_p(t)$.

$$\text{Hint: continuity equation: } \frac{\partial n_p'(x, t)}{\partial t} - \frac{1}{q} \frac{\partial J_e(x, t)}{\partial x} = g_{ext} - \frac{n_p'(x, t)}{\tau_{min}}$$

where $n_p'(x, t)$ is the excess concentration of minority carrier, $J_e(x, t)$ is the electron current density, τ_{min} is the electron carrier lifetime, g_{ext} is the net generation rate of the excited source, and n_{p0} is the electron concentration under thermal equilibrium.

6.3 An LED biased at 3.2 V with the current 20 mA. Luminous intensity of this LED is 0.3 cd (or 300 mcd). Assume this LED is a Lambertian emitter with the single emission wavelength at 470 nm. What are the current efficiency (cd/A), power efficiency (lm/W), and photon number per second, of this LED? Given $V(\lambda) = 0.09$ at 470 nm.

6.4 What is the maximum attainable luminous efficiency of D65 ($x = 0.313$, $y = 0.329$) light source by mixing LEDs (assuming each LED emits at a single wavelength)? Is it a di- or tri-chromatic white light?

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Organic light-emitting devices

7.1 Introduction

The operation principles of organic light-emitting devices (OLEDs) are similar to those of semiconductor light-emitting diodes (LEDs), as described in Chapter 6, except the materials are organic rather than semiconductor materials.¹ When a voltage is applied to such a device, holes and electrons are injected from the anode and cathode, respectively, and then recombine to emit light.

Energy states in organic materials can be described by molecular orbitals which are combinations of all the atomic orbitals. The electrons fill the molecular orbitals from the lowest energy states so that the highest occupied molecular orbital (HOMO) can be defined. Once the system is excited, the electrons can be promoted to higher molecular orbitals. The first excited state is called the lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO in organic materials are similar to the valence and conduction band in semiconductor materials, in some respects. After the carrier is excited, optically or electrically, to higher energy levels, it relaxes its energy radiatively or nonradiatively. Due to the difference in spin momentum, the singlet and triplet excited states have degenerate energy levels. Typically, the triplet state has slightly lower energy than the singlet state. Radiative recombination from the singlet and triplet states is called fluorescent and phosphorescent emission. Typically, the time constant of radiative recombination for a triplet exciton is much longer than that for a singlet one which results in the low phosphorescence efficiency at room temperature.

Charge carrier injection in organic devices is limited by the energy barriers at the metal–organic and organic–organic interfaces which are typically modeled by Richardson–Schottky (RS) thermionic emission.² Organic molecules stacked together in an amorphous form without a well-defined band structure results in a quite low mobility value, typically less than $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Carriers are ‘hopping’ among organic molecules in a disordered structure, which means the mobility value increases with applied electric field. In organic materials, since the free carrier density under thermal equilibrium is quite low, carrier transport in an organic thin film is usually described by trap-charge limited conduction (TCLC) and trap-free space-charge limited conduction (SCLC), which is the highest sustainable current in a perfect insulator.

By applying an electric field to an anthracene single crystal, Pope *et al.*³ in 1965 observed blue electroluminescence (EL). However, hundreds of volts of driving voltage were required due to the thick organic layer. The quantum efficiency (in terms of emitted photon numbers per injected carrier) was also very low due to the imbalanced charge injection and transport. In 1987, a two-layer device structure was first introduced by Tang *et al.* who utilized the thermal evaporation technique in vacuum for organic thin-film deposition in amorphous phase.⁴ Figure 7.1 shows the device structure. Since the

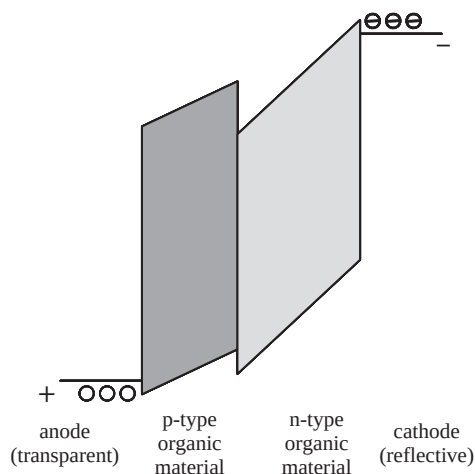


Figure 7.1 Two-layer OLED.

organic film is as thin as several tens of nanometers, the driving voltage can be less than 10 V. The two organic layers are: (1) aromatic diamine, which is used as the hole-transporting layer (HTL) material; and (2) aluminum chelate, which is used as the emitting layer (EML) and electron-transporting layer (ETL) material. Electron and hole transport in ETL and HTL is somehow similar to that in n- and p-type materials in semiconductor LEDs, with relatively high electron and hole mobilities, which recombine near the organic–organic interface. Carrier injection from the electrode to organic layer is improved by adjusting the work function of the metal electrodes. A high work function anode, indium tin oxide (ITO), and low work function cathode, Mg:Ag alloy, are hence chosen for better carrier injection. Also, since ITO is transparent to visible light, the emitted photons radiate through the anode and glass substrate, to the far field. To reduce the driving voltage, improve the quantum efficiency and extend the operation lifetime, a multilayer structure was proposed, such as a hole-injection layer (HIL), hole-blocking layer (HBL) and electron-injection layer (EIL). Emission wavelength from an OLED can be adjusted by the EML material and device structures. In 1990, Burroughes *et al.* demonstrated EL from a conjugated polymer, in a device called a polymeric light-emitting device (PLED).⁵ The operation principles of PLEDs and OLEDs are basically identical. The only difference comes from the molecular weight and fabrication technology. Conjugated polymers cannot be sublimed under vacuum due to their large molecule weight.

In this chapter, we first describe the energy diagram, the photophysical processes and the electrical properties in organic materials. Then, device structures are introduced to obtain OLEDs with better electrical and optical characteristics.

7.2 Energy states in organic materials

When two (or more) atoms come close and form a molecule, the resulting molecular orbitals and their energy states can be represented by the combination of distinct atomic orbitals. The energy diagram is shown in Figure 7.2. The lower and higher energies are called the bonding and antibonding orbitals, respectively. The bonding-state energy is less than that of the individual atoms so that the atoms tend to form a molecule.

Once the molecule is formed, the electrons fill up the molecular orbitals in order from low- to high-energy states, as shown in Figure 7.3. According to Pauli's exclusion principle, each state can accommodate two electrons with opposite spins ('up' and 'down'). Hence, we can define the HOMO,

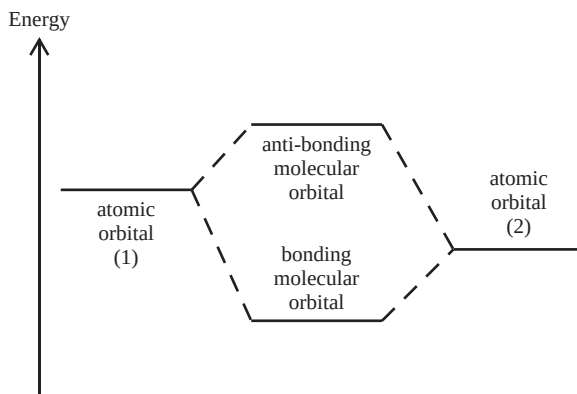


Figure 7.2 Two atomic energy states forming molecular states.⁶

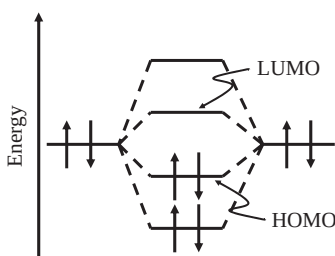


Figure 7.3 HOMO and LUMO states.

which is the ground state under thermal equilibrium. It is clear that the attractive force from the nuclei is weakest for the HOMO electrons. Hence, when there is an excitation (electrical or optical), it is possible to promote those electrons to the next higher energy state, which is the LUMO.

In general, the wave function and eigenenergy of a molecular orbital can be divided into a nuclear part and electronic part, according to the Born–Oppenheimer approximation. Since the nuclei are much heavier than the electrons, electrons can move within the framework constructed by the nuclei. Also, electrons move much faster than nuclei so that the electrons can respond instantaneously to any configuration change of the nuclei. This means that, for a given electronic state, a certain potential energy of the nuclei can be established with a distinct configuration. For a different electronic state, a different potential energy can be formed. For a more general case, i.e. three- or many-atom molecules, a potential energy ‘surface’ is needed.

7.3 Photophysical processes

Photophysical processes in organic materials include optical absorption and energy relaxation, which follow the Franck–Condon principle. Light absorption means a molecule accepts energy from an electromagnetic field. Under thermal equilibrium, the energy may be relaxed radiatively through light emission (electronic state transition), or nonradiatively through heat dissipation (such as vibrational and rotational state transition). The radiative process is very important for OLEDs and can be divided into fluorescence and phosphorescence, originating from singlet and triplet exciton relaxation. Phosphorescence emission

exhibits a spin inversion of the electron with a long carrier lifetime, and hence typically is not observable at room temperature. Unfortunately, upon electrical excitation, the number of triplet excitons is three times more than that of the singlet ones, according to quantum statistics. This means that 75 % of the excitons do not contribute to light emission in a conventional OLED. A Jablonski diagram is typically used to illustrate the whole picture of the photophysical processes, such as absorption, electronic state transition and energy relaxations, in a single molecule. When two (or more) molecules exist in a system, energy transfer may occur between the molecules. When the distance of the organic materials becomes smaller, new molecular orbitals may be created, called the excimer and exciplex, which are formed by the same or different molecules.

7.3.1 Franck–Condon principle

Photon energy absorbed by a molecule may excite the electronic, vibrational and rotational modes. Light absorption and emission in organic materials is mainly between the first excited electronic state (LUMO) and the ground electronic state (HOMO) in the ultraviolet (UV) and visible range, i.e. several electron volts. Vibrational states, i.e. several tenths of an electron volt, lie within an electronic state and there are some selection rules for energy transitions which can be distinguished from the absorption and emission spectra. Typically, rotational states are too close, i.e. several hundredths of an electron volt, to be resolved at room temperature. Figure 7.4 shows potential curves of electronic states with vibrational energy levels and wave functions. At room temperature, since energy levels for vibrational and rotational modes are very close, molecules in the ground electronic state are excited to different rotational and vibrational levels by the heat during thermal equilibrium.

Since the frequencies ($\sim 10^{15} \text{ s}^{-1}$) for electronic state excitation are much greater than nuclei vibrational motion ($\sim 10^{13} \text{ s}^{-1}$), the electronic transition must be a vertical transition in the potential curves, without any configuration change of the molecule. Also, it can be concluded that the wave function for the nuclei should be the same before and after an electronic transition. This means the vibrational wave function between two selected electronic transitions should be the same. More generally, the transition (including absorption and emission) probability of two vibrational modes in distinct electronic states is proportional to the wave function overlap of these two vibrational modes, which is called the Franck–Condon principle. For example, in Figure 7.4, when a molecule is in the ground electronic state and ground vibrational

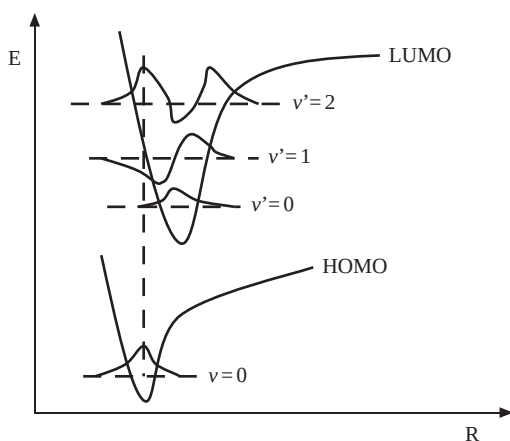


Figure 7.4 Potential curves of electronic states with vibrational energy levels and wave functions.

state ($v = 0$), it is difficult to excite it to the $v' = 0$ level since the wave function between these two vibrational modes is small. The transition $v = 0 \rightarrow v' = 1$ is possible due to partial overlap of the wave functions. The transition $v = 0 \rightarrow v' = 2$ is preferred since the wave function overlap reaches a maximum in this case.

When a molecule absorbs light an electron can be promoted to higher electronic and vibrational states; the electron can then lose some energy through vibration and rotation motions back to the ground vibrational state in the excited electronic state ($v' = 0$). Light emission can then take place, which must also follow the Frank–Condon principle. Hence, the absorption has a higher energy and a shorter wavelength than the emission, as shown in Figure 7.5(a). The difference between the absorption and emission peak is called the Stokes shift (Figure 7.5(b)). The shape of the absorption spectrum is a ‘mirror image’ of the emission one since the vibrational modes are often similar. Figure 7.5(c) shows the fluorescence (left) and absorption (right) spectra of oligophenylenevinylenes (*n*PVs) with different chain lengths in dioxane at room temperature. The structures of *n*PVs are also shown.

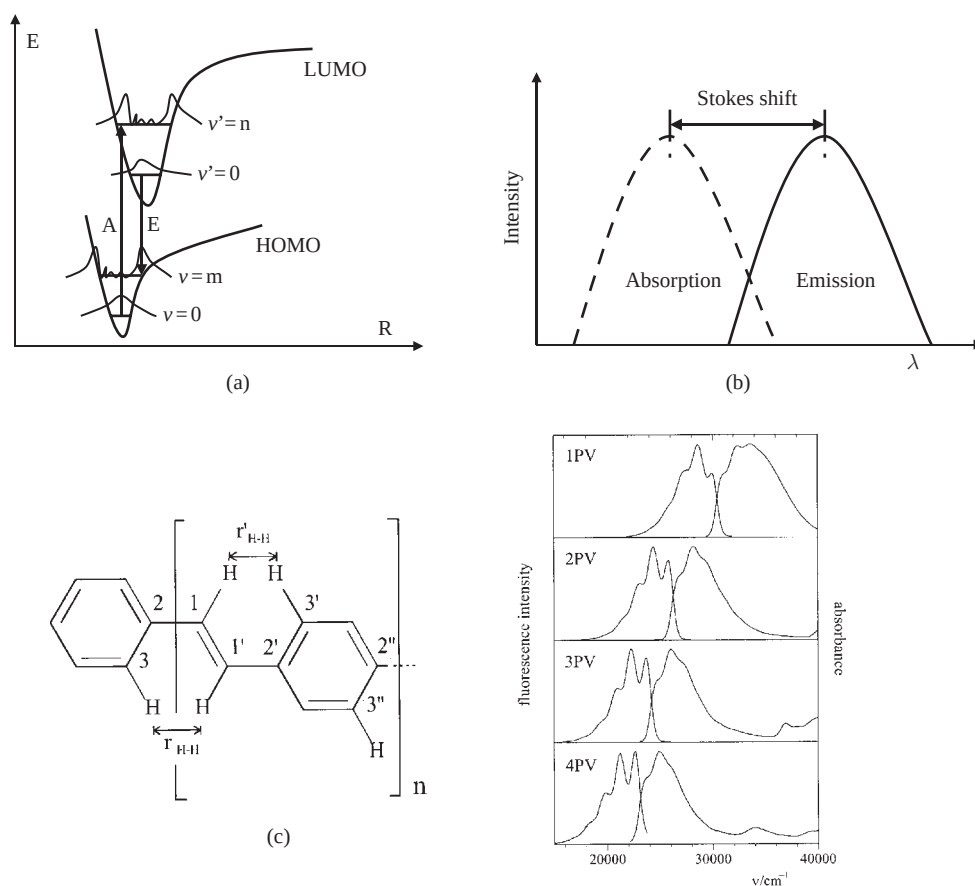


Figure 7.5 (a) Energy levels of the Stokes shift. (b) Spectra of absorption and emission. (c) Mirror image between absorption and emission spectra of *n*PVs.⁷ (Reprinted with permission from Gierschner, J., Mack, H.G., Luer, L. and Oelkrug, D. Fluorescence and absorption spectra of oligophenylenevinyls: vibronic coupling, band shapes, and solvatochromism. *J. Chem. Phys.*, **116**, 8596. Copyright (2002), American Institute of Physics)

7.3.2 Fluorescence and phosphorescence

According to the Pauli exclusion principle, two electrons in the same orbital must have opposite spins. Those two electrons are called paired electrons and the state is called the singlet ground state, denoted by S_0 in Figure 7.6. Once the molecule absorbs light, the two electrons can still have different spins in the different electronic states; this is called the singlet excited state (S_1). Since two electrons in the excited states are in different orbitals, Pauli's exclusion principle no longer applies, which means that these two electrons can have the same spin and are in the triplet state (T_1). The energy of the singlet state is higher than that of the triplet state calculated from quantum mechanics, which means energy is preferably transferred from S_1 to T_1 , together with a spin inversion. This process is called 'intersystem crossing'. Note that the triplet state must be the excited state or it conflicts with Pauli's exclusion principle. So, T_1 cannot relax back to S_0 if there is no other spin inversion. In other words, according to the Frank–Condon principle, $T_1 \rightarrow S_0$ is 'forbidden' since the wave function overlap is zero if considering the spin term and only singlet excitons can contribute to light emission.

The terms spin-up and spin-down electrons actually refer to the spin angular momentum with positive or negative components in the z -direction. The spin angular momentum is nonzero in the x - y plane, as shown in Figure 7.7(a). When there are two electrons in separate electronic states, they can be destructive or constructive, corresponding to singlet or triplet states. As shown in Figure 7.7(b), there are three possible arrangements for triplet and only one for singlet state from quantum statistics. Under electrical excitation, molecules are promoted to excited states and excitons are created. According to the discussion above, the number of triplet states is three times that of singlet states when a molecule is excited. If emission comes from singlet excitons only, the maximum internal quantum efficiency (IQE), i.e. in terms of photons per injected electron–hole pair, is only 25 %.

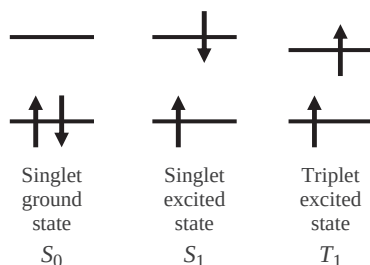


Figure 7.6 Singlet ground, singlet excited and triplet states.

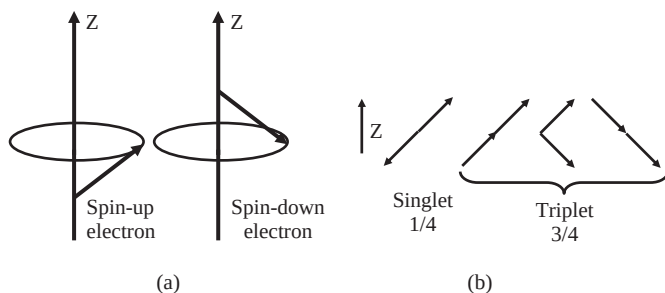


Figure 7.7 (a) Spin angular moment and (b) coupling of spin angular momenta between two electrons in different orbitals.⁸

However, the ‘allowed’ and ‘forbidden’ transitions are not so absolute in real situations since some perturbation terms are added into the total Hamiltonian which creates a mixing of spin multiplicity. Spin–orbital coupling, i.e. interaction between the spin and orbital angular momentum of an electron, is one of the most important terms which results in the mixing of singlet and triplet states. After considering the spin–orbital interaction, there are no pure singlet and triplet states. However, remember that spin–orbital coupling is only a perturbation term. This means the transition from $T_1 \rightarrow S_0$ is nonzero but still a small contribution, compared with $S_1 \rightarrow S_0$. Radiative recombinations from singlet and triplet excited states to the singlet ground state are called fluorescence and phosphorescence. Phosphorescence means the carrier lifetime is longer, because spin inversion is involved, and typically exhibits low efficiency. The strength of the spin–orbital coupling is proportional to atomic number. For an atom with a large atomic number in the molecule, spin–orbital coupling can be enhanced and the phosphorescence emission efficiency can be improved. This is called the heavy atom effect.

7.3.3 Jablonski diagram

Figure 7.8 shows a Jablonski diagram which is used to describe the energy transitions among electronic states. Figure 7.8 only shows the singlet ground state (S_0), two singlet excited states (S_1 and S_2) and two triplet excited states (T_1 and T_2). More excited states can also be included in this diagram.

As discussed above, the electron undergoes a vertical transition without changing the configuration of the nuclei due to its fast speed, and also its low weight. Absorption takes place from the singlet ground state (S_0) to the singlet excited states (S_1 and S_2). Photon energy determines the final vibrational state in the excited state and the Franck–Condon principle governs the transition probability. Then, electrons in the singlet excited state may relax their energy by release of heat through vibration and rotation. It is also possible to jump from the vibrational mode of S_2 to S_1 . Typically, energy relaxation (especially by thermal dissipation) without involving spin inversion is called internal conversion. After electrons relax their energy to the ground vibrational and rotational state of the singlet excited state S_1 , fluorescence emission takes place from S_1 to S_0 through photon emission, which has to obey the Franck–Condon principle as well. Obviously, the emission wavelength is longer than the absorption one, i.e. the Stokes shift. It is also possible to relax energy from S_1 and S_2 to S_0 by vibrational and rotational states which contributes to nonradiative recombination. Electrons in the singlet excited state can transfer to triplet

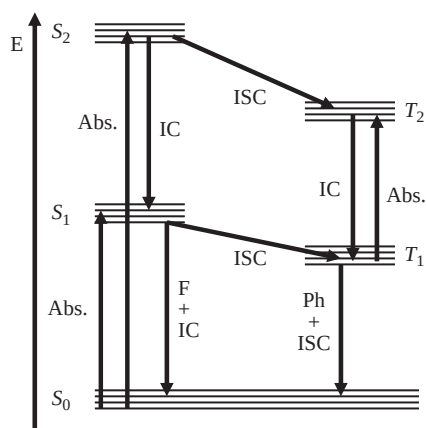


Figure 7.8 Jablonski diagram. (Abs., absorption; IC, internal conversion; ISC, intersystem crossing; F, fluorescence; Ph, phosphorescence.)

states (T_1 and T_2) via intersystem crossing. Internal conversion may happen from T_2 to T_1 . Absorption is possible between T_1 and T_2 since the two states exhibit the same spin angular momentum, which is called triplet–triplet absorption. Relaxation from T_1 and T_2 may be radiative or nonradiative. Photon emission from T_1 to S_0 is called phosphorescence, which exhibits a longer wavelength than fluorescence emission. Coupling from higher vibrational modes of T_1 (or T_2) to S_1 (or S_2) is also possible via intersystem crossing which results in delayed fluorescence emission from S_1 (or S_2) to S_0 .

7.3.4 Intermolecular processes

Not only does energy relaxation occur via intramolecular processes, as described by the Jablonski diagram, but energy transfer and relaxation also occur between molecules which are called intermolecular processes. One of the most important processes is the energy transfer from donor to acceptor materials which is most useful in OLEDs for adjusting the emission wavelength, improving the efficiency and extending the operation lifetime. When two molecules come close, new orbitals form and the emission wavelength shows a red-shift, which is called excimer and exciplex, consisting of the same or different molecules. Quenching is a kind of intermolecular energy relaxation via nonradiative recombination, which may be caused by high concentrations, metal materials or impurities.

7.3.4.1 Energy transfer process

A molecule in an excited electronic state, which is called a ‘donor’, may transfer its energy to another molecule, which is called an ‘acceptor’. After this process, the donor molecule returns to its ground electronic state and the acceptor molecule is promoted to a higher state,⁹ which can be represented as



where D and A are the donor and acceptor. The asterisk denotes the excited state. Energy transfer can be a two-step process without direct interaction between the donor and acceptor molecules as follows:



Here, photons from the radiative recombination of donor are absorbed by the acceptor and promote the acceptor to an excited state. This is called radiative energy transfer since photons are involved in this process. The strength of this energy transfer only depends on the emission efficiency of the donor and the absorption efficiency of the acceptor at this wavelength. A single process without the intermediation of photons, described by Equation (7.1), is also possible when donor and acceptor molecules are close (less than 10 nm), which is called nonradiative energy transfer, through the energetic resonance of two molecules. As shown in Figure 7.9, this process is isoenergetic and the transfer probability is proportional to the spectral overlap (J) between donor emission ($I_D(v)$) and acceptor absorption ($\epsilon_A(v)$) spectra, as follows:

$$J = \int_0^{\infty} I_D(v) \epsilon_A(v) dv. \quad (7.4)$$

Two possible mechanisms account for nonradiative energy transfer, which are dipole–dipole interaction and electron exchange, called Förster and Dexter energy transfer. The rate constant ($k_{ET(\text{Coulomb})}$) of the Förster energy transfer, which originates from dipole resonance from donor to acceptor molecules, can be represented as

$$k_{ET(\text{Coulomb})} \approx \frac{f_D f_A}{R_{DA}^6 \tilde{\nu}^2} J, \quad (7.5)$$

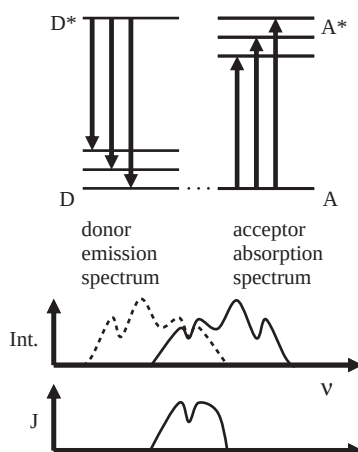


Figure 7.9 Donor emission and acceptor absorption spectra and their spectral integral.

where f_D and f_A are the transition probabilities for donor emission and acceptor absorption, following the Franck–Condon principle, and R_{DA} is the distance between donor and acceptor molecules. We can also see that the interaction strength decreases fast with increasing donor–acceptor separation. Typically, Förster energy transfer is efficient within 10 nm. Considering the spin angular momentum, the following energy transfer is allowed:



However, due to the characteristics of dipole–dipole interaction, spin inversion is impossible according to the selection rule. So the following energy transfer is forbidden:



The rate constant ($k_{ET(exchange)}$) of the Dexter energy transfer can be written as

$$k_{ET(exchange)} \approx \exp\left(\frac{-2R_{DA}}{L}\right) J, \quad (7.8)$$

which decreases exponentially with increasing donor–acceptor distance. Since it involves two electrons jumping between donor and acceptor molecules, Dexter energy transfer is a short-range process which is only effective within 1 nm. This characteristic also makes the two energy transfers allowed since the total spins are conserved:¹⁰



7.3.4.2 Excimer and exciplex formation

When two identical molecules (denoted as ‘M’ in Figure 7.10(a)) – one in its ground electronic state and the other in its excited state – come close, new electronic states with lower energy may form which can be viewed as a complex, as shown in Figure 7.10(a). It is called an ‘excimer’ (excited dimer).

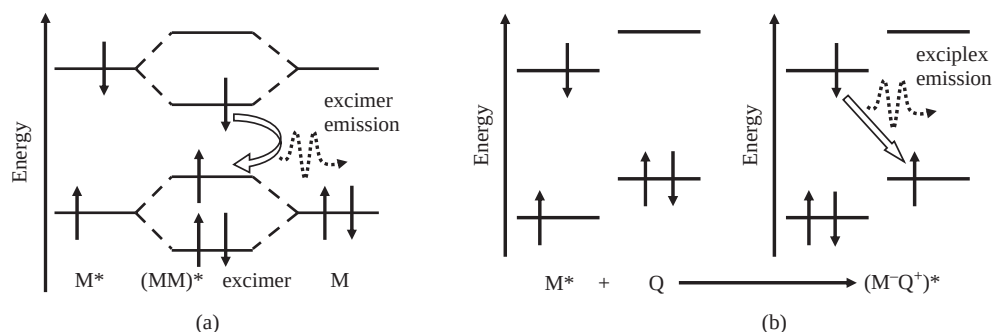


Figure 7.10 (a) Excimer and (b) exciplex formation.

Two different molecules can also form a complex (exciplex) by charge transfer process, as shown in Figure 7.10(b), where 'M' and 'Q' denote two different molecules.¹¹ Excimer and exciplex may relax their energy radiatively, back to the ground state. Note that excimers and exciplexes are bonded complexes formed only in the excited state and dissociated in the ground state.

It is straightforward to see that the emission wavelength from this excited state of the complex is greater than the original molecules due to the smaller bandgap. Figure 7.11 shows an example of excimer fluorescence.¹² Film 1 is a neat 4,4'-N,N'-dicarbazole-biphenyl (CBP) film. The absorption and photoluminescence (PL) emission peaks are at 350 and 390 nm, respectively. Since the hosts are all CBP for Films 1 to 4, the absorption spectra are nearly identical for these four films. In Film 2, with incorporation of <1 wt% of platinum(II) (2-(4',6'-difluorophenyl)pyridinato-N, C2')(2,4-pentanedionato) (FPt1) into CBP, the PL spectral peak shifts to 470 and 500 nm due to dopant emission. There is a small hump at 380 nm due to insufficient energy transfer. In Film 3, with further increase in FPt1 to 7 wt%, one can see a broad-band PL emission in the long-wavelength region (i.e. 570 nm) which arises from excimer emission. On mixing two dopant materials into CBP, i.e. 6 wt% iridium bis(4,6-difluorophenyl-pyridinato-N, C2)-picolinate (Flrpic) and 6 wt% FPt1, a white PL emission can be achieved from Film 4.

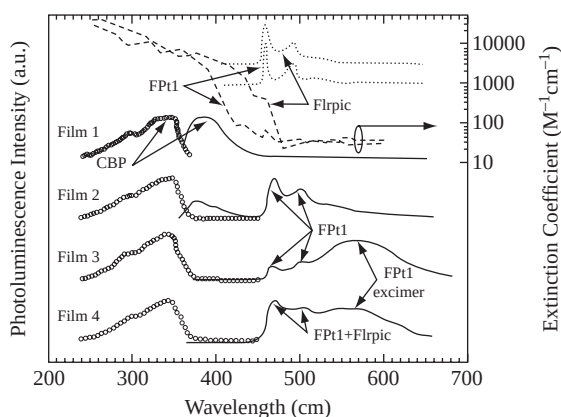


Figure 7.11 Absorption and fluorescence spectra of four films. Film 1, neat CBP; Film 2, CBP + <1 wt% FPt1; Film 3, CBP + 7 wt% FPt1; Film 4, CBP + 6 wt% FPt1 + 6 wt% Flrpic.¹²

7.3.4.3 Quenching process

Fluorescence quenching as a photophysical process can be described by



where Q is called the quencher. The quenching process is an intermolecular process in which the excited molecules relax energy through the quencher, which can be the same as or different from M , called self-quenching and concentration quenching. Excimer and exciplex relaxation may be nonradiative which is a kind of quenching process. Also, some unwanted chemicals in an organic material provide a similar energy relaxation route which is called impurity quenching. In OLEDs, generated excitons may transfer energy to the metal electrode, which is called the electrode quenching process.

7.3.5 Quantum yield calculation

From a macroscopic viewpoint, light decreases after passing through an absorptive medium. We can define the absorption coefficient (α) as

$$dI = -\alpha I dx, \quad (7.12)$$

where I and x represent the light intensity and the absorption thickness, respectively. In this equation, the intensity decrease is proportional to: (1) the absorption coefficient, (2) the incident intensity and (3) the absorption thickness. After integrating both sides over the whole sample thickness d , the resulting equation is

$$I = I_0 e^{-\alpha d}, \quad (7.13)$$

where I_0 is the initial light intensity. One can write

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \left(\frac{1}{2.303} \right) \alpha d = \epsilon c d, \quad (7.14)$$

where A is the absorbance (or optical density) of the sample, c is the concentration (in mol l^{-1}) and ϵ is the molar absorption coefficient (in $\text{l mol}^{-1} \text{cm}^{-1}$). This is called the Beer–Lambert law.

Example 7.1

Time-of-flight (TOF) is a technique which is commonly used to determine the carrier mobility in organic materials. The basic concept of TOF is to calculate the carrier drift time through a material at a given electric field across it. Carriers are generated by optical pumping. Therefore, the region of carrier generation requires a much narrower width as compared with that of carrier transport. Assume an organic material has an absorption coefficient $\alpha = 5 \times 10^5 \text{ cm}^{-1}$ at an excitation wavelength of 355 nm. Find the penetration depth of light, which can be considered the width of the carrier generation region in TOF measurement.

Answer. The penetration depth, L , of light impinging on a material is defined as the distance at which the incident intensity drops by a factor of e^{-1} . According to this definition, $L = 1/\alpha = 1/(5 \times 10^5 \text{ cm}^{-1}) = 20 \text{ nm}$. Therefore, the thickness of the materials used in TOF measurements must usually be of the order of several micrometers to make sure that the carrier drift length approximates to the thickness of the deposited material.

In a system with many particles, when carriers are promoted (optically or electrically) to the excited electronic state, the rate equation is used to describe the dynamics of relaxation back to the ground state or to other excited electronic states, as follows:

$$\frac{\partial n}{\partial t} = G(t) - \frac{n}{\tau_0}, \quad (7.15)$$

where $G(t)$ is the carrier generation rate which is used to describe the electrical or optical pumping, n is the carrier density in the excited state and τ_0 is the carrier lifetime of the excited state. This can also be written as $\tau_0 = 1/k_0$, where k_0 is the rate constant. So the decay rate of carriers in the excited state is proportional to the carrier density and the rate constant. Hence, the carrier density in the excited state (n) decays with time after being promoted at $t = 0$:

$$n(t) = n_0 \exp(k_0 t), \quad (7.16)$$

which can be used for both radiative or nonradiative relaxation.

The quantum yield of a certain relaxation process is defined as the ratio of carrier numbers involved in the process to the total carrier numbers in the excited state. From the Jablonski diagram, carriers relax through different pathways, such as fluorescence to the ground state, internal conversion and intersystem crossing, with rate constants k_F , k_{ic} and k_{isc} , respectively. The sum of the quantum yields for all processes is equal to 1. The rate equation for the first singlet excited state can be written as

$$\frac{\partial S_1}{\partial t} = G(t) - (k_F + k_{ic} + k_{isc})S_1. \quad (7.17)$$

And the quantum yield of the fluorescence (ϕ_F) is given by

$$\phi_F = \frac{k_F}{k_F + k_{ic} + k_{isc}}. \quad (7.18)$$

Example 7.2

Triplet–triplet exciton annihilation is a well-known phenomenon in phosphorescent OLEDs. The process is $T_1 + T_1 \xrightarrow{k_{TT}} T_n + S_0$ or $S_n + S_0$. Here, T (S) denotes triplet (singlet) exciton concentration, k_{TT} is the rate constant and subscripts 0 and n denote ground and n th excited state. This annihilation process is governed by

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2} - \frac{T}{\tau} - k_{TT} T^2,$$

where D is the diffusion coefficient and τ is the triplet exciton lifetime. Assume $k_{TT} = 1.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$; $\tau = 10 \text{ ms}$; and $T = 5 \times 10^{16} \text{ cm}^{-3}$. (1) Find the exciton lifetime for annihilation process. (2) Find the exciton lifetime for the entire system.

Answer. (1) Exciton lifetime is $\tau_{TT} = 1/k_{TT}T$. Obviously, the higher the triplet exciton concentration, the faster is the annihilation process. This leads to efficiency roll-off under high injection current, since the number of radiative excitons is reduced:

$$\tau_{TT} = \frac{1}{1.8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \times 5 \times 10^{16} \text{ cm}^{-3}} = 1.1 \text{ ms}.$$

(2) Exciton lifetime in the entire system is

$$\tau_{\text{total}} = \frac{1}{1/\tau + 1/\tau_{TT}} = \frac{1}{(1/10 \text{ ms}) + (1/1.1 \text{ ms})} = 0.99 \text{ ms}.$$

7.4 Carrier injection, transport and recombination

Electroluminescence (EL) of organic solids comes from the recombination of injected carriers, which is similar to the emission mechanisms of semiconductor LEDs, as described in Chapter 6. Typically, an OLED is fabricated on an indium tin oxide (ITO)-coated substrate. Thin (100–200 nm) amorphous organic layers are deposited on the ITO anode having different functions such as HIL, HTL, EML, ETL and EIL. Finally, a cathode metal is then evaporated. In an OLED, charges injected from electrodes transport through the organic layers, where they then recombine and form excitons which emit light after a transition from an excited state to the ground or an intermediate state.¹³

Fowler–Nordheim (FN) tunneling and Richardson–Shottky¹⁴ (RS) thermionic emission can be used to treat carrier injection in semiconductor devices. However, in an OLED, these can only partially describe the behavior between organic materials and organic–metal interface because of: (1) the chemical reactions that may take place between the interfaces which result in the formation of interfacial layers and (2) the disordered nature of the organic materials.

Since OLED (or PLED) thin films are amorphous without a crystalline structure, the charge transport cannot be well described by the band theory developed for semiconductors or molecular crystals. In contrast, in organic thin films, the charge carriers ‘hop’ among different localized states, which explains the low carrier mobility of organic thin films (typically $<10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹⁵ Such localization of the excited states also results in the large binding energy of excitons. For an OLED display, emission wavelengths are within the visible range. One can understand from the Stokes shift, as described in Section 7.3.1, that the absorption should be in the UV region with bandgap of $\sim 2\text{--}4 \text{ eV}$, which results in the low carrier concentrations in organic materials (typically $<10^{10} \text{ cm}^{-3}$) since it is difficult to generate ‘free’ carriers thermally. From the simple equation

$$\sigma = nq\mu, \quad (7.19)$$

where σ is the conductivity (in $(\Omega \text{ cm})^{-1}$), n is the carrier concentration, q is electronic charge (in C) and μ is the carrier mobility, one can obtain the conductivity of an organic thin film as being of the order of $10^{-12} (\Omega \text{ cm})^{-1}$. When the conductivity is between 10^{-8} and $10^2 (\Omega \text{ cm})^{-1}$, the material is called a semiconductor. Higher and lower conductivities correspond to conductors and insulators. For example, the conductivity of glass is between 10^{-11} and $10^{-10} (\Omega \text{ cm})^{-1}$, higher even than many organic thin films. From this viewpoint, organic materials for OLED applications can be regarded as more like insulators, rather than semiconductors. For practical use, the organic layer thicknesses must be very small (hundreds of nanometers) provided the driving voltage is not too high ($<10 \text{ V}$).

The carriers in organic thin films are called ‘space charges’ since free carriers are negligible, and all the carriers are injected from the electrodes. The molecules are positively or negatively charged, when the carriers are injected, which are called cation or anion, respectively. The carriers are ‘hop’¹⁶ among different molecules under the influence of an electric field. So, it is easy to understand that the mobility in an organic thin film increases with increasing electric field, which is called the Poole–Frenkel (PF)¹⁷ model. To describe carrier transport in organic thin films, time-dependent continuity equations, drift–diffusion current equation and Poisson’s equation are still valid, as described in Chapter 6. However, some modifications are needed for organic thin films. Under certain approximations, the current density–voltage relation can be described by the SCLC and TCLC. Figure 7.12 shows a typical current density (J)–voltage (V) characteristic of an OLED using a double-logarithm scale. Ohmic current, $J_{\text{ohmic}} \propto V$, dominates in region I which arises from drift of the limited free carriers inside the organic materials. With increasing the driving voltage, carriers are injected from the electrodes and transport inside the organic materials with traps which is TCLC, $J_{\text{TCLC}} \propto V^{l+1}$. This is the case of region II where the plot has a slope of $l + 1$. When the traps are filled up, it becomes SCLC, $J_{\text{SCLC}} \propto V^2$. Region III describes this phenomenon, where the slope of the J – V curve is exactly 2 for the double-logarithm scale.

The recombination rate in an OLED depends on the spatial overlap of the hole and electron densities. Since the mobility values of the organic materials are so low, as compared to the recombination time, electrons and holes recombine and form excitons as soon as they meet in the space domain, which follows

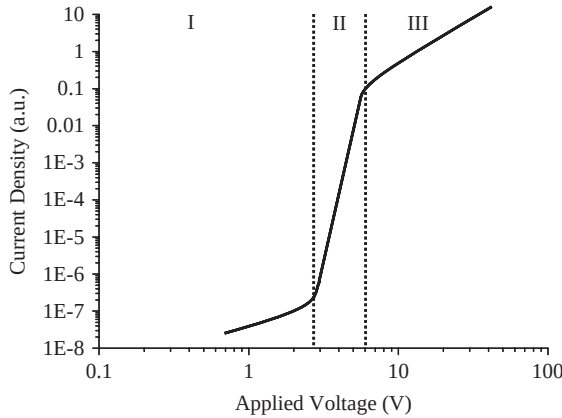


Figure 7.12 Typical J - V characteristics of an OLED.

so-called Langevin recombination, as for the LED case described in Chapter 6. Once the excitons relax their energy through radiative recombination and generate light, the electromagnetic wave propagates in the thin-film structure with thickness comparable to the emitting wavelength. The strong interference has great influence on the optical characteristics such as output intensity, spectrum and device efficiency.

7.4.1 Richardson–Schottky thermionic emission

In a one-dimensional model, one can assume an organic material with a thickness L with anode and cathode at $x = 0$ and $x = L$, respectively. The hole current injected from the anode ($x = 0$) to the organic layer can be represented by

$$J_p(0) = J_{th} - J_{ir} + J_{ptu}, \quad (7.20)$$

where J_{th} is the thermionic emission current, J_{ir} is the backflowing interface recombination current and J_{ptu} is the tunneling current.

The thermionic emission current has the well-known form¹⁸

$$J_{th} = A^* T^2 \exp\left(\frac{-E_b}{\eta kT}\right), \quad (7.21)$$

where A^* is Richardson's constant, E_b is the interfacial energy barrier and η is the ideality factor, the value of which is typically between 1 and 2 for semiconductors.¹ Because of the image force, E_b depends on the electric field at the interface:

$$E_b = \phi_B - \sqrt{\frac{q|F(0)|}{4\pi\epsilon}}, \quad (7.22)$$

where ϕ_B is the Schottky energy barrier at zero field and $|F(0)|$ is the electric field at the interface. In Figure 7.13(a), the image charge and the electric field line at the metal–organic interface is shown, and the barrier energy level change due to the image force is also shown in Figure 7.13(b).

The interface recombination current is proportional to the hole density at the interface:¹⁸

$$J_{ir} = qvp(0) \quad (7.23)$$

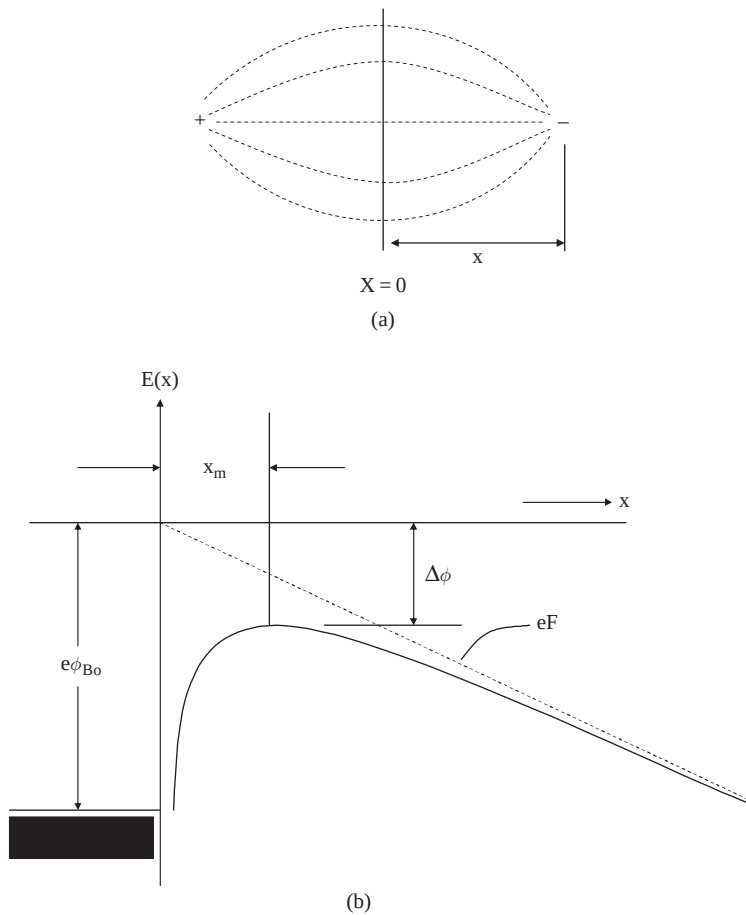


Figure 7.13 (a) Image charge and the electric field line at the interface.¹⁹ (b) Energy level change due to image force.

The kinetic coefficient ν is determined by detailed balance between thermionic and interface recombination:¹⁸

$$\nu = \frac{A^* T^2}{qn_0}. \quad (7.24)$$

Parameter n_0 is the densities of states; we take the densities of states as $1.0 \times 10^{21} \text{ cm}^{-3}$ for organic materials.^{18, 20}

The FN injection for the tunneling contact is²¹

$$J_{\text{ptu}} = \frac{q^3}{8\pi h E_b} |F|^2 \exp\left(-\frac{8\pi\sqrt{2m^*E_b^3}}{3qh|F|}\right), \quad (7.25)$$

where m^* is the effective mass of the carrier and h is Planck's constant. Equations similar to (7.24) and (7.25) can be written for the electron current density. Typically, in an OLED, thermionic emission and FN tunneling (field emission)²² govern the injection mechanism at high and low field conditions.

7.4.2 SCLC, TCLC and PF mobility

The transport of electrons and holes in an OLED is described by time-dependent continuity equations, with a drift–diffusion current, coupled to Poisson’s equation.¹⁸ Considering electron transport in a unipolar organic material without generation and recombination, the continuity equations can be written as

$$\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x}, \quad (7.26)$$

where J_n is the electron current density and n is the electron density, as described in Chapter 6. Under steady state, $\partial/\partial t = 0$,

$$J_n = \text{const.} \quad (7.27)$$

As described above, carrier density in organic materials is negligible under thermal equilibrium, which means the diffusion current can be neglected. So, only the drift term appears in the current density equation:

$$J_n = nq\mu E \quad (7.28)$$

or

$$n = \frac{J_n}{q\mu E}, \quad (7.29)$$

where E is the electric field, μ_n is the electron mobility and q is the electronic charge. Coupled with the Poisson equation:

$$\frac{\partial E}{\partial x} = -\frac{q}{\varepsilon} n \quad (7.30)$$

or

$$\frac{\partial E}{\partial x} = -\frac{q}{\varepsilon} \frac{J_n}{q\mu E}, \quad (7.31)$$

where ε is the static dielectric constant. Assuming μ is a constant, one can obtain the relation between current and electric field, and applied voltage since $V = \int E \, dx$, which is the well-known Mott–Gurney equation to describe the SCLC:

$$J_{\text{SCLC}} = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{d^3}, \quad (7.32)$$

where d is the layer thickness.

The physical meaning of SCLC is that it represents the maximum possible unipolar current that a perfect insulator without trap, i.e. organic materials, can sustain at a given potential difference. In the presence of traps, the current will increase faster than quadratic until all traps are filled. In this regard, TCLC deals with the carrier transport in the bulk, which is governed by²³

$$J_{\text{TCLC}} \propto \frac{V^{l+1}}{d^{2l+1}},$$

where l represents the effects of traps. For example, an increase of $(l + 1)$ directly indicates increasing of the trap depth and density. In general, the TCLC model is well used in the low electric field condition, whereas the SCLC is simply sufficient for high electric field. This observation implies that at lower fields, charge carrier traps are involved, which are filled up at higher field. Because of the nature of localization of π -electrons in organic molecules, carrier transport in a solid-state organic layer can be seen as ‘hopping’ between molecular sites. The ‘hopping’ process is essentially a one-electron oxidation–reduction process between neutral molecules and their charged derivatives. The charge hopping rate is known to be not only influenced by the effects of disorder, but also strongly dependent on applied electric field. This

phenomenon directly leads to field-dependent carrier mobility, which is governed by a well-known rule called the PF model.²⁴ The PF mobility, which is very frequently observed in amorphous molecular materials, is

$$\mu(F) = \mu_0 \exp(\beta\sqrt{F}). \quad (7.33)$$

where μ_0 is the zero-field mobility and β is a material related parameter.

7.4.3 Charge recombination

Recombination radiation from organic solids is defined as light emission following the fusion of oppositely charged carriers into an electrically neutral state. Following recombination of opposite carriers, excitons are created, which undergo one-dimensional diffusion towards the electrodes. As described above, carrier mobility values in organic materials are much slower than the recombination rate, which means electrons and holes recombine simultaneously when they meet in the space domain. Hence, the recombination process in an OLED is typically described as a bimolecular process, following the Langevin theory, which is governed by

$$R = \gamma np, \quad (7.34)$$

where R is the carrier recombination rate, n (p) is the electron (hole) density and γ is the recombination coefficient of the organic materials. The exciton migration is not affected by applied voltage since it is neutral. The exciton diffusion is forbidden in the material with larger exciton energy. The exciton diffusion length (L) with a typical value of several nanometers, which roughly defines the width of the recombination zone, is related to the exciton diffusion coefficient (D) and its lifetime (τ)²⁵ by

$$L = \sqrt{D\tau}. \quad (7.35)$$

As discussed in Section 7.3.2, only singlet excitons are generated using optical excitation because of the spin conservation. For electrical excitation, the injection of electrons and holes is followed by the formation of free polarons, which is the deformation of the molecule due to injected carriers. When they experience opposite coulombic attraction, a neutral bound polaron pair, or charge transfer (CT) states are created.²⁶ With electric excitation, the rate of singlet CT (¹CT) and triplet CT (³CT) state generation obeys simple statistics, thus leading to a ratio of 1:3. The transfer between both types of exciton is governed by intersystem crossing (ISC). The CT states will sequentially transfer to their respective lowest excited Frenkel excitons. The relaxation of singlet excitons to the ground state via radiative decay is called fluorescence, whereas that of triplet excitons is called phosphorescence. In fluorescent organic materials, only singlet excitons, electrically generated excitons of 25 %, are exploited for light emission and the remaining 75 % are relaxed through nonradiative paths.²⁷ To effectively release all available excitons via radiation relaxation, phosphorescent materials are employed to develop highly efficient OLEDs.^{28–31}

7.4.4 Electromagnetic wave radiation

As in the case of LEDs in Chapter 6, from classical viewpoints, the emission from organic thin films can be considered as a point source and it has a radiation cone defined by Snell's law which only takes account of the refractive index of the organic thin films and air.³² Considering the unit sphere shown in Figure 7.14, the shaded region enclosed by the critical angle at the interface of organic material and glass indicates the exit through which the generated photons can escape.

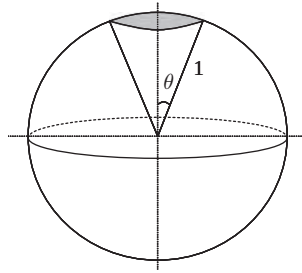


Figure 7.14 Escape cone from an OLED.

For an organic layer with refractive index of n_{EML} , the fraction of generated light escaping from the substrate (which is defined as the external quantum efficiency) can be calculated from³³

$$\begin{aligned} \eta_c &= \frac{2 \int_0^{\theta_{\text{EML-air}}} 1 \times d\theta \times 2\pi \times 1 \times \sin \theta}{4\pi \times 1^2} = \int_0^{\theta_{\text{EML-air}}} \sin \theta d\theta = 1 - \cos \theta_{\text{EML-air}} \\ &= 1 - \frac{\sqrt{n_{\text{EML}}^2 - 1}}{n_{\text{EML}}} = 1 - \sqrt{1 - \frac{1}{n_{\text{EML}}^2}} \cong \frac{1}{2n_{\text{EML}}^2}, \end{aligned} \quad (7.36)$$

where η_c is the extraction efficiency and $\cos \theta_{\text{EML-air}}$ is the organic–air critical angle. For example, n_{EML} is typically 1.6, which means the extraction efficiency is only about 20 % and 80 % of photons are trapped inside the OLED. However, a multilayer OLED cannot be described by the ray optics model since the layers have thicknesses less than the wavelength of the emitted light. The ray optics description cannot completely explain the optical characteristics in an OLED. An example is the dependence of far-field emission pattern on the thickness of the organic layer, which cannot be explained by classical theory.

By using a transfer matrix method, the optical interference effect in thin-film structures can be well described. The photon emission from organic materials originates from the dipole oscillations. Typically, an OLED consists of a transparent anode with ITO, organic layers and a reflective cathode on the glass substrate, as shown in Figure 7.15. Photons generated in the organic layers propagate out of the OLED through the ITO anode and the glass substrate.

Such a structure can be regarded as a Fabry–Perot cavity and the emission spectrum in the normal direction can be described by the equation³⁴

$$|E_{\text{out}}^{\text{up}}(\lambda)|^2 = |E_{\text{in}}(\lambda)|^2 \times \frac{T_2[1 + R_1 + 2\sqrt{R_1} \cos(4\pi x/\lambda)]}{1 + R_1 R_2 - 2\sqrt{R_1 R_2} \cos(4\pi L/\lambda)}, \quad (7.37)$$

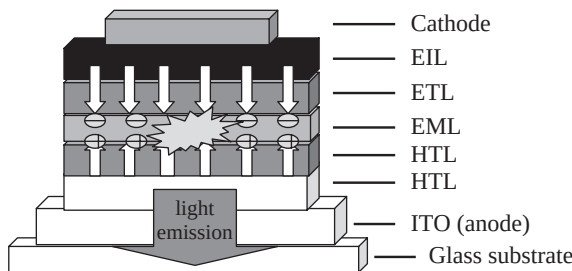


Figure 7.15 Typical OLED structure.

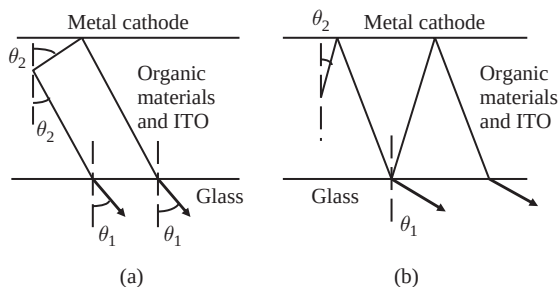


Figure 7.16 Schematic of (a) wide-angle and (b) multiple-beam interference.

where the term on the left-hand side is the output intensity, the first term on the right-hand side is the free-space EL intensity, x is the effective distance of a dipole from the reflective cathode and R_1 is the reflectivity of the cathode. Also, R_2 and T_2 are the effective reflectivity and transmittivity of the ITO anode side, respectively. L is the total optical thickness of the cavity, given by

$$L = \left| \frac{\varphi_{\text{an}} \lambda}{4\pi} \right| + \sum_j n_j L_j + \left| \frac{\varphi_{\text{ca}} \lambda}{4\pi} \right|. \quad (7.38)$$

Here, n_j and L_j are the refractive index and thickness of the j th layer between the two electrodes, φ_{ca} is the phase shift corresponding to the effective reflectivity R_1 and φ_{an} is the phase shift corresponding to the effective reflectivity R_2 at the interface between the organic materials and the anode.

Equation (7.37) can be rewritten as

$$|E_{\text{out}}^{\text{up}}(\lambda)|^2 = |E_{\text{in}}(\lambda)|^2 \times Tr \times [1 + R_1 + 2\sqrt{R_1} \cos(4\pi x/\lambda)] \quad (7.39)$$

with

$$Tr = \frac{T_2}{1 + R_1 R_2 - 2\sqrt{R_1 R_2} \cos(4\pi L/\lambda)}. \quad (7.40)$$

The term $[1 + R_1 + 2\sqrt{R_1} \cos(4\pi x/\lambda)]$ represents the antinode enhancement factor of the wide-angle interference, as shown in Figure 7.16(a).³⁵ It has a maximum value when the emitting dipoles are located exactly at the antinode of the standing wave within the microcavity. The term Tr accounts for the effect of multibeam reflective interference, as shown in Figure 7.16(b).³⁶ We can see that the effect of the wide-angle interference is determined only by the dipole position and the cathode reflectivity, while that of the multibeam reflective interference is controlled by the cavity optical length and anode and cathode reflectivities.

7.5 Structure, fabrication and characterization

Considerations for device design in a small-molecule or polymer OLED include the electrical and optical optimization. For reducing the driving voltage, carrier injection should be efficient, which means careful energy level alignment is needed. Also, the mobility value should be as high as possible, and the free carrier density should be improved. For improving the recombination rate, suitable energy barriers are needed in the device to confine the carriers, which resemble heterojunction structures in a semiconductor LED. Sometimes, it is difficult to find an organic material with good electrical properties and high efficiency. Organic mixtures, or guest–host (dopant–matrix) systems, are introduced to improve the IQE. Since the planar geometry of an OLED of hundreds of nanometers in thickness is a microcavity

structure, optical interference has to be taken into consideration for maximizing the external quantum efficiency. In a small-molecule OLED, precise control of the thin-film deposition enables multilayer structures to be possible. However, in a polymer OLED, a multilayer structure is difficult to accomplish by solution process. The thin-film process is the only difference in fabrication for the small-molecule and polymer OLED. The patterned process before and the encapsulation process after thin-film deposition are nearly identical for the small-molecule and polymer OLED. To drive a display, passive matrix (PM) and active matrix (AM) techniques are typically used, as for liquid crystal displays (LCDs). However, there are still some differences since the OLED is a current-driven device, rather than a capacitor as in the case of a LCD. For example, at least two transistors and one capacitor are needed in a pixel for AM driving. Lifetime is one of the main issues for OLED applications, which can be classified as extrinsic and intrinsic degradation. With a proper encapsulation (or passivation) process and careful environmental control during fabrication, extrinsic degradation can be greatly reduced. However, intrinsic degradation from organic material degradation dominates the ultimate operation lifetime of an OLED.

7.5.1 Device structure

The basic structure of an OLED is a layer structure in which the organic layer(s) is (are) sandwiched by two electrodes. Typically, ITO with a high transparency and work function is used as the anode. Then, one or more organic thin films are formed (by evaporation, spin-coating, ink-jet printing, etc., which is discussed in Section 7.5.3.1) followed by a metal cathode. The simplest structure is to use a single organic layer between the electrodes, as shown in Figure 7.17.³⁷ In such a structure, the work functions of the anode and cathode should be matched to the HOMO and LUMO of the organic material, for better carrier injection. The organic material should exhibit ambipolar transport characteristics and emission capability.

Typically, it is difficult to find a bipolar organic material with high emission efficiency. Even if an organic material does exhibit such good electrical and optical characteristics, the recombination zone in such a device is not easy to control for highly efficient emission. For example, if recombination takes place near the electrode, which means the dipole oscillation is at the node, rather than the antinode position (Section 7.4.4), then this leads to destructive interference and decreases the device efficiency, called electrode quench. To improve this, two- or multilayer structures are introduced with their functions of carrier injection, transport, and emission.

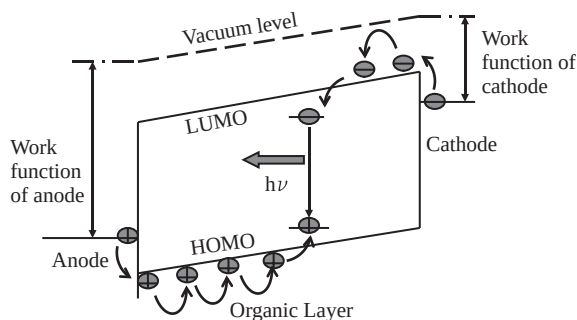


Figure 7.17 Device structure of a single-layer OLED.

7.5.1.1 Two-layer OLED

Figure 7.18 shows the device structure of a two-layer OLED, first introduced by Tang *et al.*⁴ The two organic layers are aromatic diamine and aluminum chelate (tris(8-hydroxyquinoline) aluminum, Alq₃) which are the HTL and ETL, respectively. Different from the bipolar characteristics in the single-layer device, HTL and ETL only transport unipolar carriers, holes and electrons. This provides some flexibility in selection of organic materials. Also, this structure helps to improve the device efficiency due to better carrier confinement. In this two-layer structure, carrier recombination occurs near the HTL–ETL interface. Since the HTL and ETL are different organic materials, such a structure is similar to the heterojunction in semiconductor LEDs. Under forward bias, electrons from the cathode will drift from the ETL and be blocked at the HTL–ETL interface since the LUMO value of the HTL is typically lower than that of the ETL. The HOMO value of the ETL is slightly larger than that of the HTL so that holes can readily enter into the ETL. The low hole mobility in the ETL results in high hole concentration inside the ETL and near the HTL–ETL interface. This enhances the collision capture process and recombination occurs in the ETL. So this is the EML at the same time. The interface between these two materials confines the carriers near the interface when applying an electrical field and increases recombination probability. The recombination zone is in the ETL within 10 nm of this interface.³⁸

Typically, the electron mobility in the ETL is at least one order of magnitude lower than the hole mobility in the HTL ($\mu_{e,ETL} \ll \mu_{h,HTL}$), which means there are many holes waiting in the HTL–EML interface for recombination. The recombination probability (P_R) is given by

$$P_R = \left(1 + \frac{\tau_{rec}}{\tau_t}\right)^{-1}, \quad (7.41)$$

where τ_{rec} is the carrier recombination time and τ_t is carrier transit time of the electrons from the cathode to the HTL–EML interface. Equation (7.41) can be rewritten as

$$P_R = \left(1 + \frac{w}{d_c}\right)^{-1}, \quad (7.42)$$

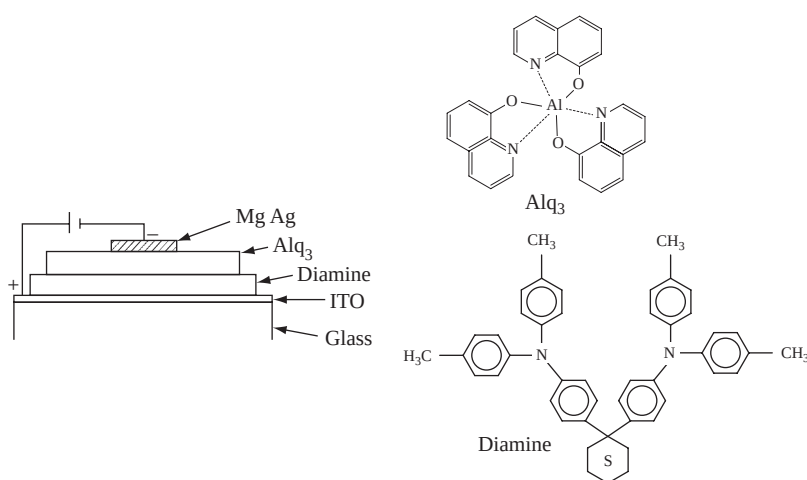


Figure 7.18 Layer structure and organic materials of the first two-layer OLED.⁴ (Reprinted with permission from Tang, C.W. and Vanslyke, S.A. Organic electroluminescent diodes. *Appl. Phys. Lett.*, **51**, 913. Copyright (1987), American Institute of Physics)

where w and d_e are width of recombination and the ETL thickness, respectively, due to the barrier confinement.³⁹ From this equation, we note that a narrow recombination width is preferred for preventing leakage of holes and electrons toward electrodes, which leads to low efficiency. Also, we also note that transparent ITO was used as the anode and reflective Mg:Ag alloy was used as the cathode. Work functions of anode and cathode should be high and low, for better hole and electron injection. The transparency of the ITO should be high since the photons radiate out through the anode and glass.

Figure 7.19(a) shows the curves of current density and EL intensity versus voltage. The driving voltage is about 8 V with a current density of 100 mA cm^{-2} . Compared with a conventional semiconductor LED, the current density reaches 200 mA cm^{-2} only at 4 V.⁴ In this OLED, the HTL and ETL thicknesses are 75 and 60 nm, respectively, which are much thinner than the epitaxy layer (several micrometers) of a semiconductor LED. Although the device thickness is one order of magnitude greater than that of semiconductor LEDs, the driving voltage is more than two times higher due to the high resistivity of the organic materials. Figure 7.19(b) shows the EL spectrum of this device with a full width at half-maximum of about 100 nm which is two times broader than that of semiconductor devices due to more vibrational and rotational modes in the organic materials.

7.5.1.2 Dopant in the matrix as the EML

In the two-layer structure, recombination occurs at the ETL, which means the ETL is also the EML. So the functions of this layer include carrier transport and emission. However, sometimes it is difficult, although possible, to find an organic material (high emission efficiency and high carrier mobility) for the whole visible range. A common way to solve this problem is to introduce an additional material into the EML as a guest-host system, which is a high-efficiency organic material doped into a transporting material as the EML.⁹ The criteria of the transporting material in the EML, which is usually called the matrix (or the host), include that it: (1) exhibits good carrier transport characteristics and (2) has suitable energy levels for carrier trapping and/or good overlap between host PL and dopant absorption spectra for efficient energy transfer, as described in Section 7.3.4. For a dopant (or the guest) material, high efficiency is a basic requirement. Not only does this improve the electrical and optical characteristics of an OLED, but the guest-host system also effectively prolongs the stability of a device by transferring recombined excitons to the emissive and stable dopant site thus minimizing nonradiative decay.⁴⁰

Figure 7.20(a) shows the device structure proposed by Shi and Tang and the component molecular structures.⁴⁰ Copper phthalocyanine (CuPC), N,N' -diphenyl- N,N' -bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine

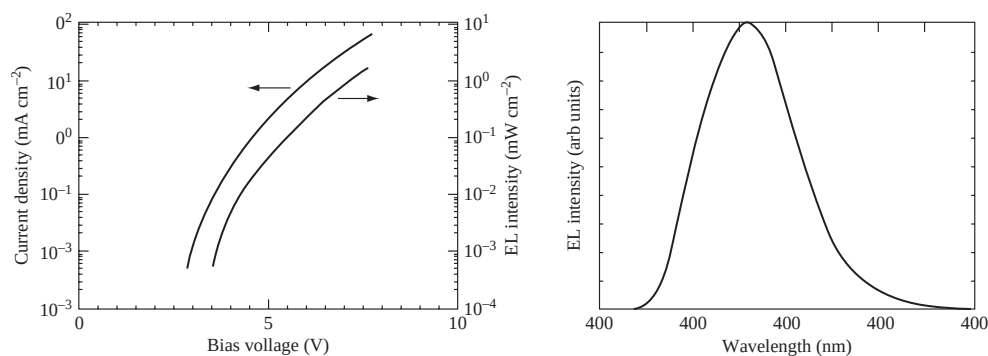


Figure 7.19 (a) J - L - V curves and (b) EL spectrum of the two-layer OLED.⁴ (Reprinted with permission from Tang, C.W. and Vanslyke, S.A. Organic electroluminescent diodes. *Appl. Phys. Lett.*, **51**, 913. Copyright (1987), American Institute of Physics)

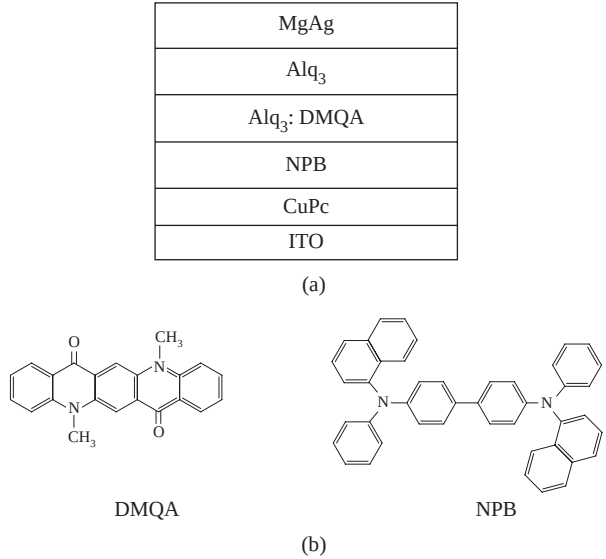


Figure 7.20 (a) Device structure and (b) molecular structures of a guest–host system.⁴⁰ (Reprinted with permission from Shi, J. and Tang, C.W. Doped organic electroluminescent devices with improved stability. *Appl. Phys. Lett.*, **70**, 1665. Copyright (1997), American Institute of Physics)

(NPB) and Alq₃ are the HIL, HTL and ETL, respectively. A detailed description of the HIL is given in Section 7.5.1.3. In this device, the EML consists of a mixture of Alq₃ and *N,N*-dimethylquinacridone (DMQA), which exhibits high emission efficiency. DMQA concentration should be low enough to keep the molecules apart from each other to prevent excimer quenching (Section 7.3.4). On the other hand, when the dopant concentration is not high enough, the intermolecular energy transfer is not efficient since the distance between the host and dopant is too great.

Table 7.1 shows the device performances with different DMQA concentrations. It can be seen that the luminance increases then decreases with increasing the dopant concentration. The first increase results from the higher efficiency of DMQA than Alq₃. And the decrease comes from excimer quenching, also called concentration quenching. We also note that the operation lifetime increases with the incorporation of the dopant since higher radiative emission means lower heat generation, which is beneficial to lifetime extension (Section 7.5.5). Emission wavelength and the CIE coordinates of the doped and undoped materials are similar, which is within the green region. One of the most well-known green dopants

Table 7.1 Device performances with different dopant concentrations.⁴⁰

DMQA (%)	0.00	0.26	0.40	0.80	1.40	2.50
Lum. output (cd m ⁻²)	518	1147	1322	1462	1287	1027
Efficiency (cd A ⁻¹)	2.59	5.74	6.61	7.31	6.44	5.14
CIE _x	0.3872	0.3876	0.3785	0.3922	0.4046	0.4095
CIE _y	0.5469	0.5858	0.5995	0.5901	0.5799	0.5742
EL peak (nm)	544	540	540	544	544	544
T _{1/2} (h)	4200	7335	7500	7340	5450	3650

Adapted with permission from Shi, J. and Tang, C.W. Doped organic electroluminescent devices with improved stability. *Appl. Phys. Lett.*, **70**, 1665. Copyright (1997), American Institute of Physics.

recently used in OLEDs is 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1 *H*,5*H*11*H*-[*l*]benzopyrano[6,7,8-*ij*]quinolizin-11-one (C545T), which is a derivative of a class of highly fluorescent coumarin laser dyes.⁴¹

In addition to improvement of efficiency and lifetime, color tuning is also an important function of guest–dopant systems. By suitable molecular design, it is possible to emit different colors of light with different dopant materials even with the same host. For example, by doping the laser dye molecule DCM1 in Alq₃, a quantum efficiency of about 2.3 % can be obtained with the EL peak at 600 nm.⁹ With suitable molecular modification, another red dopant material, 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran, known as DCJTb, has been synthesized.⁴² The efficiency of the red OLED based on DCJTb:Alq₃ EML can reach 2.0 cd A⁻¹ with luminance of 400 cd m⁻² at a current density of 20 mA cm⁻².

One of the criteria for efficient energy transfer from the host to the dopant materials is good spectral overlap between the host PL and the dopant absorption, which implies the dopant should have a larger bandgap than the dopant. This means that it is not applicable to use Alq₃ as the host for blue OLEDs. Since OLEDs emit at shorter wavelength and hence higher photon energy than red and green devices, a wide-bandgap material is required to provide such a high energy. For better energy transfer, a larger bandgap of the host material as compared to that of the dopant is needed. The host material in the EML also has to match the HOMO/LUMO levels for effective energy transfer and charge injection from HTL and ETL. The details of several combinations of guest–host systems have been published. Examples are using distyrylarylene (DSA) derivative as the emitting host material and DSA amine styrylamine 4,4'-bis(2-(9-ethyl-9*H*-carbazol-3-yl)vinyl)biphenyl (BCzVBi) as the emitting dopant⁴³ and doping 2,5,8,11-tetra(*t*-butyl)-perylene (TBP) into the diphenylanthracene derivatives 9,10-di(2-naphthyl)anthracene (ADN). Related researches are ongoing.

7.5.1.3 HIL, EIL and p-i-n structure

As described above, HTL and ETL materials have high carrier mobilities and can transport holes and electrons, for recombination in the EML. Organic materials with high fluorescence quantum efficiency are used as the EML, which determines the emission color. To further improve the hole and electron injection capability from anode and cathode to the organic layers, HIL and EIL are incorporated in OLEDs. A HIL having HOMO level between that of ITO and HTL is used to help the holes inject from the ITO anode into the HTL. Likewise, EIL having LOMO level close to ETL is used to help the electrons inject from the cathode into the ETL.

Figure 7.21 shows an example of the insertion of a HIL, 4,4',4''-tris(3-methylphenyl)phenylamino]tri-phenylamine (m-MTDATA), between the HTL 4,4'-bis(3-methylphenyl)phenylamino)biphenyl (TPD) and an ITO anode.⁴⁴ From Equations (7.21) and (7.22), we can see that the current density from thermionic emission decreases exponentially with increasing barrier height. The HOMO value of m-MTDATA is 0.1 eV higher than the work function of ITO and 0.4 eV lower than the HOMO of TPD, which forms a 'ladder-like' structure for better hole injection from the ITO to the HTL. Molecular structures and energy diagram are shown in Figures 7.21(a) and (b). From Figure 7.21(d), we note that the luminance at a constant current density is highest in the three-layer structure (HIL/HTL/ETL) of device C, due to better hole injection. When the conventional HTL was replaced by m-MTDATA (device A), the efficiency is lowest since the barrier for hole injection to the EML is highest. Another function of the HIL is to prevent the oxygen from the ITO attacking the organic layer (Section 7.5.5) which extends the lifetime. A copper phthalocyanine (CuPc) layer is used for this purpose. And this improves balances in hole and electron recombination which is a very important parameter for enhancing quantum efficiency in OLEDs.

From another viewpoint, the work function of the electrode could also be engineered to improve the injection capability. Figure 7.22 shows surface treatment at the ITO surface. If the anode is treated with acid (Figure 7.22(a)), it will attract the negative charges which form a surface dipole towards the organic

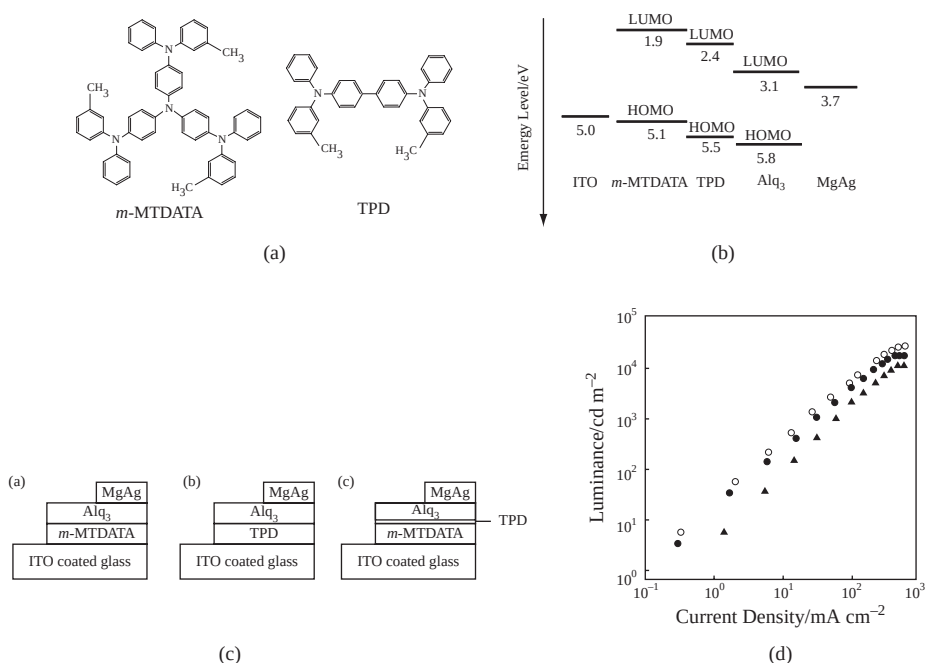


Figure 7.21 (a) Molecular structures, (b) energy level diagram, (c) device structures and (d) luminance versus current density curves.⁴⁴ (Reprinted with permission from Shirota, Y. *et al.*, Multilayered organic electroluminescent device using a novel starburst molecule, 4,4',4''-tris(3-methylphenylphenylamino) triphenylamine, as a hole transport material. *Appl. Phys. Lett.*, **65**, 807. Copyright (1994), American Institute of Physics)

layer, which accelerates the holes from the ITO into the organic layers. Typically, such a surface dipole is represented as the shift of the vacuum levels or the increase of the work function of the anode surface. Due to the vacuum level misalignment, the effective barrier between the ITO and the HOMO of the organic layer is reduced. On the other hand, as shown in Figure 7.22(b), the effective barrier increases which impedes the hole injection by base modification. Dipping the ITO substrate into acid solution is a method to improve the hole injection capability. Another common way is to use an oxygen plasma or UV-ozone

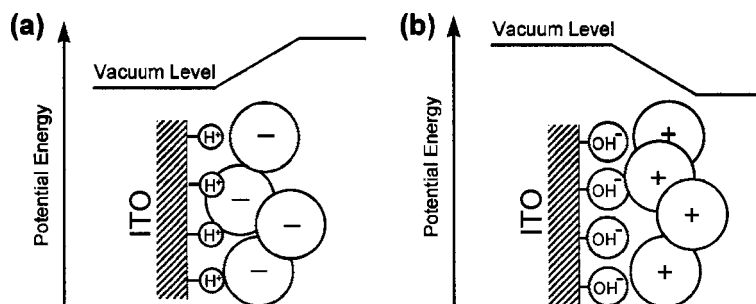


Figure 7.22 (a) Acid and (b) base treatment at the ITO surface.⁴⁷ (Reprinted with permission from Nuesch, F., Rothberg, L.J., Forsythe, E.W. *et al.*, A photoelectron spectroscopy study on the indium tin oxide treatment by acids and bases. *Appl. Phys. Lett.*, **74**, 880. Copyright (1999), American Institute of Physics)

treatment before depositing the organic layers.^{45, 46} The oxygen plasma can not only effectively increase the work function of ITO, but also remove hydrocarbon contaminants on the as-grown ITO substrate.

The work function of the cathode should be as low as possible for better electron injection. Figure 7.23 shows the current density versus voltage of OLEDs with different cathode structures. Devices with aluminum cathodes exhibit the highest driving voltage (17 V) at 100 mA cm⁻². By replacing the Mg_{0.9}Ag_{0.1} alloy as the cathode material, a 4 V reduction in driving voltage is achieved due to the lower work function. In this alloy, a small amount of silver is added to improve the stability against the environment and form better adhesion to the organic layers.⁴ Although low work function materials, such as alkali metals and alkaline earth metals, are preferred for the cathode, they are reactive under typical environments containing oxygen and water, which increases the difficulties in device processing and material handling. An alternative is to deposit an ultrathin and insulating layer, such as LiF, between the air-stable metal, such as aluminum, and the organic layers.^{48, 49} Details of the physical mechanism are not clear yet. One of the most popular explanations is that the LiF decomposes into lithium and fluorine upon aluminum evaporation. Then lithium penetrates into the organic layer which forms radical anions and effectively increases the electron concentration in the ETL. Also, it forms dipole layers in the organic–cathode interface which facilitate electron injection. However, due to the insulating characteristics, thinner or thicker LiF layers result in voltage increase, as shown in Figure 7.23.

In addition to the energy mismatch and the low mobility, the high driving voltage of OLEDs also arises from the low free carrier concentrations of organic materials. The p- and n-type doping technology, with the concept similar to that in semiconductor LEDs, is introduced. For the p-type doping, a HTL material is usually doped with a Lewis acid, which attracts electrons and free holes are generated. This shifts the Fermi level in the organic materials from the center of the bandgap to close to the HOMO, which improves the hole transport capability. Also, due to the increase of the carrier concentration, the Fermi level alignment between the electrode and the p-doped organic layer results in an ohmic-like injection

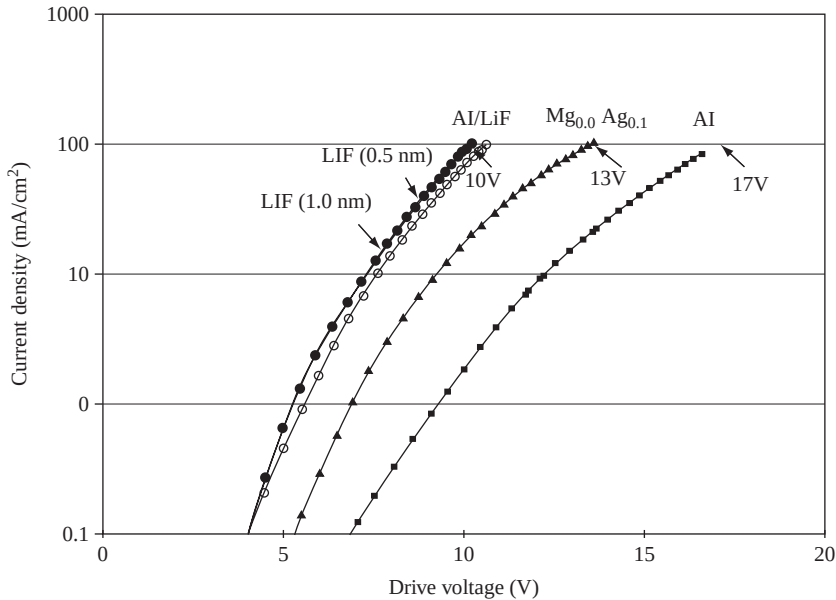


Figure 7.23 Plots of log J versus V curves of OLEDs with different cathode materials.⁵⁰ Reprinted with permission from L.S. Hung, C.W. Tang, and M.G. Mason, Enhanced electron injection in organic electroluminescence devices using an Al/LiF electrode. *Appl. Phys. Lett.*, 70, 152. Copyright (1997), American Institute of Physics.

property at the interface, which facilitates hole injection. Some effective candidates of guest–host systems for p-type organic materials include doping tetracyanoquinodimethane (TCNQ) derivatives,⁵¹ V_2O_5 or $FeCl_3$ into zinc phthalocyanine (ZnPC) or arylamine derivatives.⁵² In contrast to p-type doping, n-type molecular doping is more difficult due to the requirement of the HOMO value of the dopant being smaller than the LUMO of the host for providing the free electrons, which makes such materials unstable against oxygen.⁵³ An alternative approach is the use of alkali metals like lithium, sodium or cesium doped into organic materials, which is called the metal dopant (MD) technique.⁵⁴ These metals easily release a free electron to the organic host for conducting. With such a MD technique, not only can carrier transport characteristics be much improved by n-type doping, but the interface between the electrode and organic material can also be modified from Schottky barrier to ohmic contact which helps carrier injection and voltage reduction. By applying the p- and n-type doping techniques, p–i–n OLEDs can be fabricated with a low driving voltage and higher power efficiency.⁵⁵ However, the strong acid and base characteristics of the p- and n-type doping sometimes lead to difficulties in fabrication. Also, the operation lifetime of MD technology is still an issue since it is easy for the metal to diffuse into the EML as an exciton quencher during operation.⁵⁶

7.5.1.4 Top-emission and transparent OLEDs

Typically, an OLED has a transparent ITO anode and a reflective cathode, with high and low work functions. For improving the flexibility in the design of the driving circuit (Section 7.5.3.3) and external quantum efficiency (Section 7.7), top-emission and transparent OLEDs have been fabricated. By replacing the reflective cathode with a transparent conductive layer (e.g. ITO), a see-through display can be achieved. However, since the work function of ITO is high (~ 4.7 eV), which is not suitable for electron injection, a suitable buffer layer between the ETL and ITO ‘cathode’ is needed for better carrier injection capability. Such an opaque buffer layer must be thin enough to provide high transmittance. Mg:Ag and LiF/Al bi-layer of several nanometers thickness is suitable for this application due to the good electron injection capability. Another function of the buffer layer is to protect the organic layers during the fabrication of the ITO ‘cathode’, where a sputter process is needed. Although there is a buffer layer in such a device, the radio-frequency power of the sputtered ITO cathode has to be controlled very carefully in order to decrease the energetic ion damages to the underlying organic layer. Under this process condition, the deposition rate is usually as low as several angstroms per second. The optical transmittance of the buffer layers is one of the major concerns in such an architecture. A thicker buffer layer absorbs more light and hence decreases the OLED luminance and transmittance. On the other hand, a thinner buffer layer may not be enough to protect against sputtering damage. However, a thick ITO cathode, several hundred nanometers, is necessary for reducing the ohmic loss due to the low conductivity of ITO, i.e. around 10^4 S cm⁻¹. Such a conductivity value is one to two orders of magnitude less than those of metal materials. Hence, a thin and semitransparent metal material formed by thermal evaporation can be used as the transparent or semitransparent cathode. Such a thin cathode of 20–30 nm thick can be samarium,⁵⁷ Ca/Mg⁵⁸ and LiF/Al/Ag.⁵⁹

For a top-emission OLED, which means light comes out from the top side rather from the substrate side, a reflective anode is also needed. Deposition of a reflective metal, such as silver, underneath the ITO is straightforward.⁶⁰ Some high work function metals, such as gold and titanium, are good candidates, in terms of injection capability. A high reflectivity over the whole visible range is also needed for better optical characteristics. Oxidation of silver produces AgO_x with a high work function which forms an effective HIL, while the silver provides good electrical characteristics at the same time.⁵⁹ In a top-emission OLED, the reflective anode and the semitransparent cathode form a microcavity which exhibits a strong multibeam interference (Section 7.4.4). Riel and coworkers fabricated a top-emission OLED with a dielectric layer of ZnSe capped on the semitransparent cathode, as shown in Figure 7.24(a).⁶¹ They demonstrated that the EL intensity and spectral characteristics are a function of dielectric thickness, as

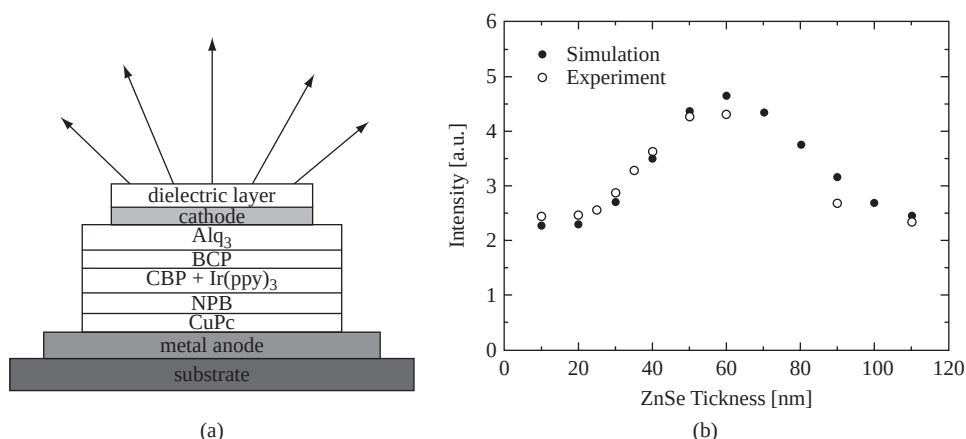


Figure 7.24 (a) Schematic of a top-emission OLED with dielectric layer (ZnSe) and (b) experimental and simulated intensity in the normal direction.⁶¹ (Reprinted with permission from Riel, H., Karg, S., Beierlein, T. and Rieß, W., Tuning the emission characteristics of top-emitting organic light-emitting devices by means of a dielectric capping layer: an experimental and theoretical study. *J. Appl Phys.*, **94**, 5290. Copyright (2003), American Institute of Physics)

shown in Figure 7.24(b). The dielectric layer can enhance the outcoupling light intensity in the forward direction. Also, angle-independent spectra can be achieved by tuning the dielectric thickness.

By engineering the transparent, semitransparent and reflective characteristics of the electrodes, some interesting displays can be fabricated. Based on the transparent OLED, the display can show information from the both sides.⁶² Moreover, a double-sided OLED display with different content is also possible by engineering the optical characteristics of the electrode.⁶³ A potential application for such a display is in clam-shape mobile phones, which need two displays. Here, one double-sided display can replace the two displays, and possibly the backlight unit, which can greatly reduce the thickness of the mobile phone.

7.5.2 Polymer OLEDs

When distinguished by molecular weight, there are two main kinds of OLEDs. For a molecular weight less than 1000 g mol⁻¹, the device is called a small-molecule OLED, which can usually be thermally evaporated under high vacuum. For a molecular weight over 10 000 g mol⁻¹, the device is called a polymer OLED (or polymeric light-emitting device, PLED).

In 1990, a polymer OLED was fabricated by Burroughes *et al.*⁵ using the spin-coating technique. A thin film of poly(*p*-phenylene vinylene) (PPV) with yellowish-green emission was used with a device configuration of Al/Al₂O₃/PPV/Al. The emitting spectra and efficiency of the conjugate polymer can be tuned by suitable molecular design. Figure 7.25 shows some common repeating units of polymer EL materials, such as polyphenylenes (PPP), polyfluorene (PF) and PPV. In 1991, Braun and Heeger reported a red

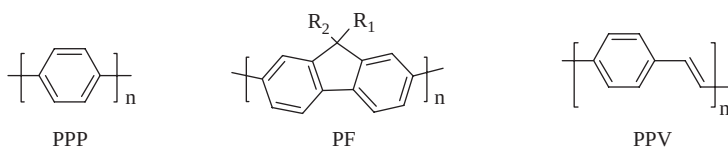


Figure 7.25 Molecular structures of some polymer EL materials.

polymer LED containing poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV).⁶⁴ Ohmori *et al.* reported a blue-emitting polymer LED, containing poly(9,9-dialkylfluorene)s, with an EL peak emission wavelength of 470 nm.⁶⁵

The long-chain characteristics of polymer molecules provide lots of flexibility for chemists to design molecules to improve the carrier transport characteristics and recombination coefficient, and to adjust the emission wavelength spanning the whole visible range. The driving voltage of polymer OLEDs is typically lower than that of small-molecule ones due to the higher conductivity. Also, the uniformity of polymer films can be greatly improved by suitable molecule design, which decreases the recrystallization phenomenon which is sometimes observed in amorphous thin films in small-molecule OLEDs.

Since the polymer will be decomposed upon thermal treatment before it obtains enough kinetic energy for evaporation, thin-film formation of polymer OLEDs is by the solution process. This consists of dissolving the polymer into solution and then coating the solution on the substrate. The solvent is vaporized under vacuum or by thermal treatment, and the polymer thin film is formed. Residual solvent in the organic thin film is sometimes an impurity quencher which results in nonradiative recombination. Also, it diffuses during device operation or storage, which shortens the device lifetime. To achieve low driving voltage, high recombination efficiency and high emission efficiency, a multilayer structure is typically desired for optimizing the optical and electrical characteristics in an OLED. However, it is not easy (although possible) to fabricate a polymer OLED with more than two layers. Since typical organic nonpolar solvents will dissolve most EL polymers, it is common to apply PEDOT:PSS, which can be dissolved in a polar solution (water soluble), as the HIL and HTL prior the EL polymer thin-film formation. Several methods have been proposed to fabricate a multilayer polymer OLED. Self-assembly methods⁶⁶ or electropolymerization provide options to avoid the solubility problem.⁶⁷ Another approach is to have a series of functional polymers that could be spin-coated on the substrate. This requires polymers that are soluble in polar and nonpolar orthogonal solvent systems.⁶⁸

7.5.3 Device fabrication

Since OLEDs and PLEDs are sensitive to moisture and oxygen, the thin-film process should be carried out in vacuum or inert gas environments. After the organic thin-film formation, the sample should be encapsulated or passivated without exposure to the ambient environment. Hence, for an OLED display, the circuitry fabricated by conventional semiconductor processes (e.g. lithography, etching and deposition) should be produced before the thin-film process.

Typically, a conventional OLED is fabricated on a glass substrate. The transparent conductive material ITO can be used as the anode. Light emission from the organic layers propagates through the transparent ITO and glass substrate. However, the resistivity of ITO is typically $10^{-4} \Omega \text{ cm}^{-1}$ which is one to two order of magnitude higher than that of the reflective metals, such as aluminum and silver, and this high resistance results in voltage drops of the ITO transmission lines, which in turn induces: (1) nonuniformity of panel luminance and (2) delay and distortion of the control signals. Hence, some assisting anode, such as aluminum or chromium, could be used outside the emission region to improve the current conduction. Since the conductivities of organic materials are quite low, the current pathways are only in the vertical direction (perpendicular to the glass substrate) and will not propagate horizontally (parallel to the glass substrate), which means the light emission occurs at the regions where anode and cathode overlap observed from the vertical direction. An insulation layer, such as polyimide, is needed to define the pattern of the emission region on the ITO and beneath the organic layers. Such a layer is critical since it provides a flat surface and buries the circuitry underneath which is important for OLED thin film deposition due to its very thin nature (100–200 nm). Thin-film transistors (TFTs) may be needed for AM driving techniques. In an OLED display, at least two TFTs in one pixel are needed due to the diode junction characteristics. Mobility of the transistors should be as high as possible to provide sufficient current, i.e. electron–hole pairs, for photon generation. Mobility decrease and threshold shift are two typical phenomena observed in TFT degradation due to the current stress.

Once the backbone of the OLED display is fabricated, the organic thin-film and encapsulation processes should be accomplished without exposure to the ambient environment. For small-molecule OLEDs, the organic materials can be sublimed through thermal evaporation under high vacuum. By controlling the temperature, the deposition rate, of as low as 0.1 nm s^{-1} , can be controlled precisely. For polymer materials, due to their large molecular weight, solution processes are needed. Two common fabrication methods are spin-coating and ink-jet printing. After film formation, the devices are transferred for encapsulation under inert environments for longer lifetime. Depositing passivation layer(s) upon the OLED directly is also possible which is beneficial for reducing the thickness of the display and has potential for flexible substrate applications.

7.5.3.1 Thin-film formation

For small-molecule OLEDs, a common method to deposit the organic thin film is by thermal evaporation under high vacuum, since the molecular weight is low enough for sublimation. As illustrated in Figure 7.26, the organic layers and the cathode materials are deposited sequentially on the patterned ITO glass substrate. Since there is no wet process allowed after the thin-film deposition, the patterns of the organic layers and the metal are defined by the shadow mask, which is positioned near to the glass substrate. This is a metal plate with holes, where the organic vapor from the thermal sources can pass through and deposit on the substrate. Typically, the substrate is kept at room temperature, which means the evaporated molecules cannot obtain enough kinetic energy to move on the glass substrate and distribute randomly in an amorphous manner. An amorphous thin film is important for better surface uniformity. The deposition rate is controlled by the evaporation temperature. Higher temperature results in faster deposition rate, and higher throughput. Device performances, such as efficiency and lifetime, are also dependent on the deposition rate.⁶⁹ However, when the deposition temperature is too high, organic material may decompose which results in material degradation and device failure. To obtain a uniform thin film, the distance between the substrate and the organic source should be as large as possible, which results in a low usage rate of the organic material. Typically, only 10 % or less is deposited on the glass substrate, while the other 90 % or so of materials are coated on the wall of the chamber. This not only wastes the organic material, but also limits the panel size. A linear source, which is a combination of ‘point’ thermal sources as a ‘linear’ one, can effectively reduce the size of the chamber, increase the material usage rate, improve the throughput and enlarge the substrate size (as large as $1100 \text{ mm} \times 1250 \text{ mm}$; Gen V glass substrate).⁷⁰

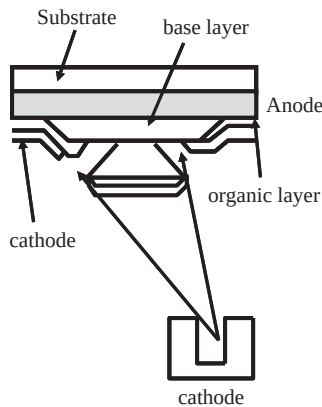


Figure 7.26 Thermal evaporation.

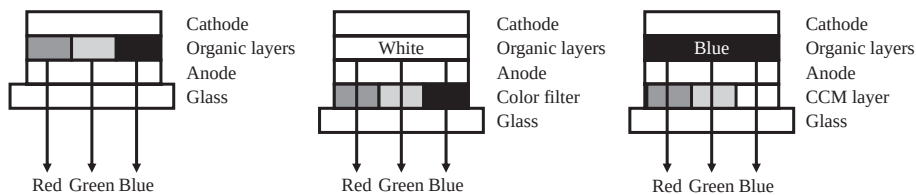


Figure 7.27 Fabrication methods for full-color OLED: (a) lateral emitter, (b) white OLED with color filter and (c) color change material (CCM).

For a full-color display, red, green and blue subpixels are needed. It is straightforward to use red, green and blue OLEDs for this purpose. However, as discussed above, the conventional lithography process is not available for OLED thin-film formation. Typically, there are three fabrication methods for full-color OLED displays (Figure 7.27): (1) use of a lateral emitter, (2) use of a white OLED with color filters and (3) use of a blue OLED with color change materials (CCMs).

As shown in Figure 7.28, lateral emitter involves depositing red, green and blue OLEDs in different zones though fine-pitch shadow masks. Device efficiency and operation lifetime is higher for lateral emitter, compared with the other two fabrication methods, since the OLEDs for three primary colors can be optimized independently. However, typically, the subpixel pitch is about 70 μm , which means the shadow mask cannot be too thick ($\sim 100 \mu\text{m}$). Since the glass substrate is as large as $370 \times 470 \text{ mm}$ (Gen II glass), it is not easy for handling and processing. When the shadow mask is used continuously for a long time (e.g. a week), the accumulation of the evaporated organic materials near the hole edge of the fine-pitch shadow mask may reduce the hole size, which in turn results in dimension reduction and misalignment of the deposited region. Also, the thermal expansion of the metal shadow mask may also result in misalignment in the high-temperature deposition environment. The distance between the

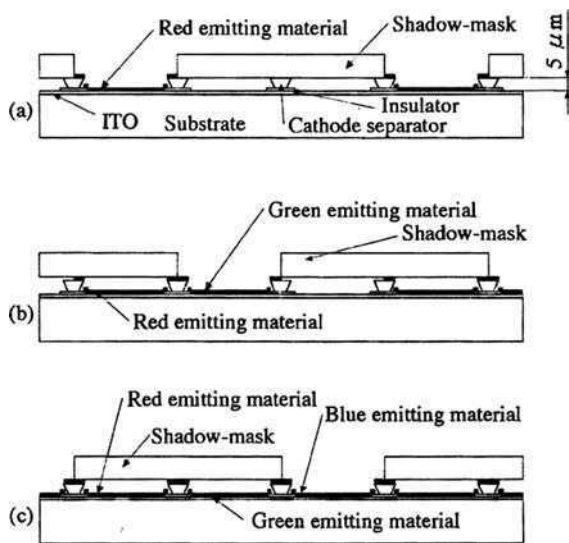


Figure 7.28 Fine-pitch shadow mask for a full-color OLED.¹³ (Reprinted from Hung, L.S. and Chen, C.H., Recent progress of molecular organic electroluminescent materials and devices. *Mater. Sci. Eng. R* **39**, 143. Copyright (2002), with permission from Elsevier)

shadow mask and the substrate should be kept small for better alignment. However, the surface of the substrate is easily scratched by the shadow mask if they are too close, which results in difficulties in device fabrication.

To simplify the process, the conventional color filter technique, as used for LCDs, can be used for full-color OLEDs. By fabricating a white OLED, without a complex fine-pitch shadow mask, and blocking the light through color filters at each subpixel can effectively improve the fabrication yield. However, similar to the case of LCDs, two-thirds of the light is absorbed by the color filter, which means the efficiency and lifetime will decrease. Operation lifetime describes the luminance decay with time, which is often different for different colors of OLEDs. For the lateral emitter, different degradation rate may result in a color shift with time. However, the color stability remains good when using a white OLED with color filter. Another possible way to improve the efficiency and simplify the fabrication is by using a CCM, which can absorb blue light, and generate red and green light. As shown in Figure 7.27, EL from the blue OLED itself is used for the blue subpixel. By using appropriate CCMs on the other two subpixels, red and green light can be generated. However, material selection, fabrication process and material stability still remain issues for this technique.

By using the laser-assisted pattern technique, a high resolution and large-size substrate can be realized at the same time with the lateral emitter arrangement.⁷¹ Laser-induced thermal imaging (LITI) is one of the most important fabrication technologies; its operation principle is shown in Figure 7.29. An organic thin film is first deposited uniformly on a donor film. Then, upon laser illumination on certain regions, light-to-heat conversion (LTHC) absorbs the light and converts it to heat, which induces the thermal expansion of the LTHC with high spatial resolution, and in turn releases the organic thin film onto the substrate. The resolution of this technology depends on the beam size of the laser beam. Limitation of the substrate size comes from the moving distances of the laser head. By increasing the numbers of laser heads, the throughput can be increased. Displays with resolution of 302 ppi and glass substrate of 730 mm × 920 mm (Gen IV) have been demonstrated with LITI technology. Also, Sony Corporation has demonstrated a 27.3-inch OLED display with full-HD resolution (1920 × 1080) using laser-induced pattern-wise sublimation (LIPS) technology.⁷² However, since the film formation process is different from that of thermal evaporation, the operation lifetime of OLEDs formed using laser-assisted patterning is sometimes shorter.

The fabrication methods for polymer OLEDs must be ‘solution’ processes since the materials cannot be sublimed due to their high molecular weight. When these materials are heated, they decompose before they obtain enough kinetic energy for sublimation. Chloroform, dichloroethane, toluene and xylene are commonly used solvents. After dissolving the polymer materials into the solvent, the solution is spin-coated or

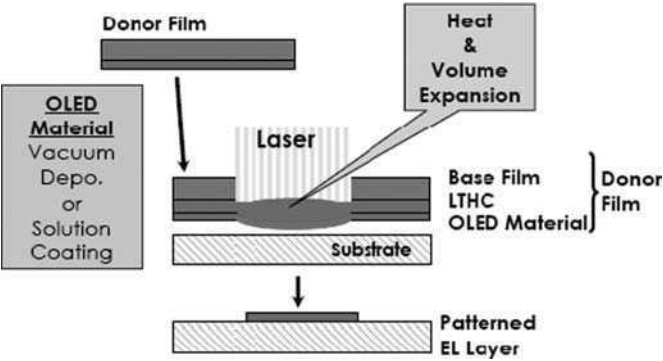


Figure 7.29 Schematic of the LITI process.⁷¹ (Source: Lee, S.T. *et al.* (2007) LITI (laser induced thermal imaging) technology for high-resolution and large-sized AMOLED. *SID Tech. Dig.*, 1588. Reproduced by permission of SID)

ink-jet printed onto the substrates. By drying off (e.g. under vacuum or heating) the solution, polymer thin films can be obtained. Spin-coating is a common method for semiconductor fabrication. By controlling the rotational rate and viscosity of the solution, thin films with precise thickness (resolution of several nanometers) can be obtained. For full-color fabrication, different solutions can be cast in different positions. Ink-jet printing, which is a conventional process in printing technology, can be used.⁷³ Seiko Epson Corporation has demonstrated a 40-inch polymer OLED display using multi-head ink-jet printing technology.

7.5.3.2 Encapsulation and passivation

Many organic materials are sensitive to moisture and oxygen. Also, the oxidation of metal electrodes may degrade the OLED properties.⁷⁴ Therefore, the isolation of the OLED from oxygen and water is necessary for lifetime extension. Typically, OLEDs are hermetically sealed with another cover using an adhesive such as UV-cured epoxy, as shown in Figure 7.30. The cover can be another glass, or a metal lid. Possible pathways for environmental moisture and oxygen are from the adhesive and the boundary of the adhesive and the glass substrate or the cover. To reduce water and oxygen permeability into the OLED, the gap between the substrate and the cover should be as small as possible to reduce the 'channel width'. At the same time, the width of the epoxy should be as wide as possible to increase the 'channel length'. Also, the interface of the epoxy with glass substrate and cover may form a channel if the bonding strength is not good enough. Even though the epoxy can entirely prevent attack from the environments, there are still possible residual solvents from the fabrication prior to the thin-film deposition, which will vaporize gradually and degrade the OLED. Hence, a desiccant such as CaO is incorporated to react with any water which is residual or diffuses through epoxy seal, as shown in Figure 7.30.⁷⁵

It is also possible to replace the cover with a passivation layer directly upon the OLED of several micrometers thickness. In this way the thickness of the display can be reduced to that of about one glass substrate (~ 0.55 mm). Also, the process flow of OLED fabrication becomes simpler. Since the organic materials cannot resist high temperature, a process temperature lower than 100°C is needed for the passivation layer. This passivation layer should not have cracks or pinholes which provide the channels for environmental attack. The thermal stress should be as small as possible so that the organic and metal thin films underneath are not damaged. Recent research has provided several concepts to form good passivation layers with low water vapor permeation rate (WVPR), such as the deposition of polymer by PECVD,⁷⁶ single adhesive layer with an inorganic cap,⁷⁷ multiple layers consisting of repeatable organic/inorganic structure⁷⁸ and the incorporation of desiccant and barrier layer.⁷⁵ The main advantages of using a polymer as passivation layer are mechanical and chemical stability and strong adhesion to the underlying layer.⁷⁶ The merits of inorganic materials are transparency and abrasion resistance. However, a low WVPR is only achieved using a thick layer (hundreds of micrometers), which results in a large mechanical stress that can crack the film beneath the passivation layer. To reduce the stress without increasing the WVPR, an adhesive layer is prepared before the deposition of the inorganic passivation layer.⁷⁷ The formation of pinholes is inevitable in a thick inorganic passivation layer. So, to fabricate

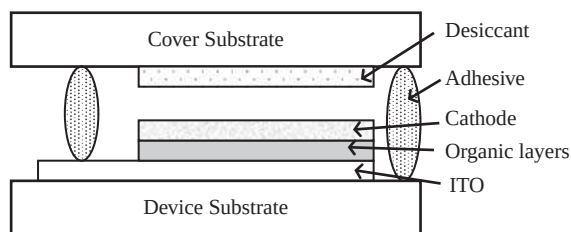


Figure 7.30 Encapsulated OLED.

a pinhole-free film and block the passage of water vapor through grain boundaries, inorganic/organic multiple layers are adopted.^{74, 79, 80}

Such a passivation layer not only can be deposited on the OLED, but also on a flexible substrate, e.g. poly(ethylene terephthalate) (PET), to reduce the WVPR from 10^{-1} – 10^1 g m⁻² per day down to levels to meet the requirements of OLEDs ($<5 \times 10^{-6}$ g m⁻² per day for a storage lifetime longer than 10 000 h).⁷⁶ Simultaneously, the surface roughness of the flexible substrate, which yields dark spots after the fabrication process, is modified by the application of multilayer structure. The height of spikes on the PET surface is reduced from 150 to <10 Å. By embedding getter particles into the polymer substrate or polymer lid, it is possible not only to block water vapor from outside, but also to absorb it before it contacts the device.

7.5.3.3 Device structures for AM driving

As discussed in Chapter 3, silicon-based TFTs on AM backplanes are a sensitive to visible light which should be shielded by a black matrix. This means some pixel size would be sacrificed without emitting light for the TFT layout. So the aperture ratio of an AM-OLED is typically low, as shown in Figure 7.31(a), which results in low display luminance. This would be even worse if more than two transistors were used. Top emission is one of the most promising technologies for achieving high aperture ratio AM-OLEDs, as shown in Figure 7.31(b).⁸¹ Typically, a top-emission OLED has a high reflective anode and a semitransparent or transparent cathode. Hence, light comes out from the semitransparent cathode side. The TFTs can be hidden underneath the reflective anode and hence the aperture ratio is increased. As shown in Equations (3.17) and (3.18), increasing the W/L value can increase the current density. Since the TFT and OLED are stacked together without interference, the whole pixel area can be used for the TFT. Hence, it is possible to use an amorphous silicon (a-Si) TFT to drive an OLED even though the mobility value is low. However, the fabrication process and the optical design of such a device are quite different from those of a conventional bottom-emission OLED. Degradation of a-Si TFTs under current stress is another issue which needs to be considered. Configurations of TFTs and OLEDs for AM-OLED displays are still being developed.

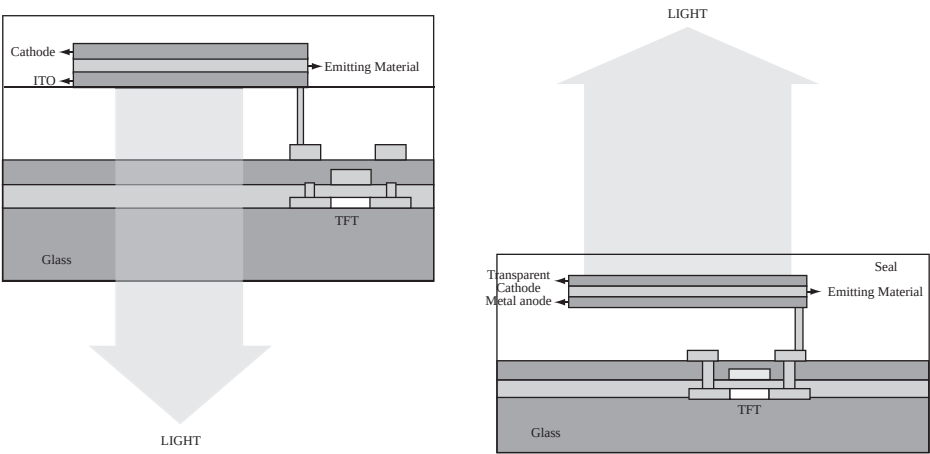


Figure 7.31 Cross-section of an AM-OLED: (a) bottom-emission and (b) top-emission OLED configuration.⁸¹ (Reprinted from Lee, C.J., Podo, R.B., Moon, D.G. and Han, J.I., Realization of an efficient top emission organic light-emitting device with novel electrodes. *Thin Solid Films*, **467**, 201. Copyright (2004), with permission from Elsevier)

7.5.4 Electrical and optical characteristics

In this section, the J – V characteristics and the optical performances of a two-layer OLED are demonstrated and analyzed, experimentally and numerically. The HTL and ETL (EML) materials are NPB and Alq₃, respectively. Their device band diagram are shown in Figure 7.32.

Five two-layer OLEDs are fabricated with varying HTL and ETL thicknesses. The HTL thickness varies from 200 to 1000 Å, at a step of 200 Å, while the ETL thickness varies from 1000 to 200 Å in order to keep the total organic thickness at 1200 Å. Table 7.2 shows the device configuration.

Figure 7.33 shows the J – V characteristics of the experimental and simulated results. We note that the current density increases sharply with increasing driving voltage, which is a typical SCLC and TCLC behavior. The driving voltage of device 1 is highest, and decreases with thicker HTL materials. The electron and hole mobilities of Alq₃ and NPB are 10^{-6} – 10^{-3} and 10^{-4} – 10^{-3} cm²/V⁻¹ s⁻¹, respectively, at a field strength of 0.1–1 MV cm⁻¹. This means that hole transport is much faster than electron transport. This also implies the electric field mainly drops across at the Alq₃ layer because of its low electron mobility.

Figure 7.34 shows the distributions of charge density and recombination rate of devices 1, 3 and 5. We can see that many holes and electrons are blocked at the HTL–ETL interface due to the energy barriers of LUMO and HOMO value differences between NPB and Alq₃, respectively. Note that the barrier for holes (0.3 eV) is smaller than that for electrons (0.6 eV) which means the holes can penetrate into the ETL, to recombine with the electrons, as shown in Figures 7.34(a)–(c). Such a carrier pile-up near the HTL–ETL interface confines the carriers, which increases the recombination efficiency. Figures 7.34(d)–(f) show the recombination rate (R), which follows Langevin theory. We can also see that the recombination mainly takes place in the ETL and neat HTL–EML interface due to the carrier pile-up.

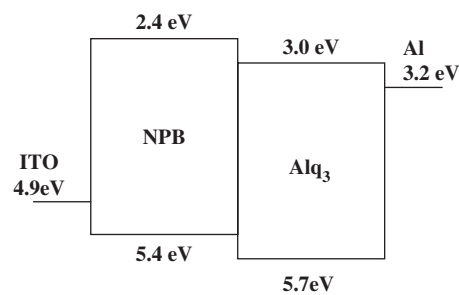


Figure 7.32 Energy diagram of the two-layer OLED.

Table 7.2 Layer structures of the two-layer OLEDs.

Unit		HTL (NPB) (Å)	ETL (Alq ₃) (Å)	LiF (Å)	Al (Å)
1	ITO glass	200	1000	12	1500
2	ITO glass	400	800	12	1500
3	ITO glass	600	600	12	1500
4	ITO glass	800	400	12	1500
5	ITO glass	1000	200	12	1500

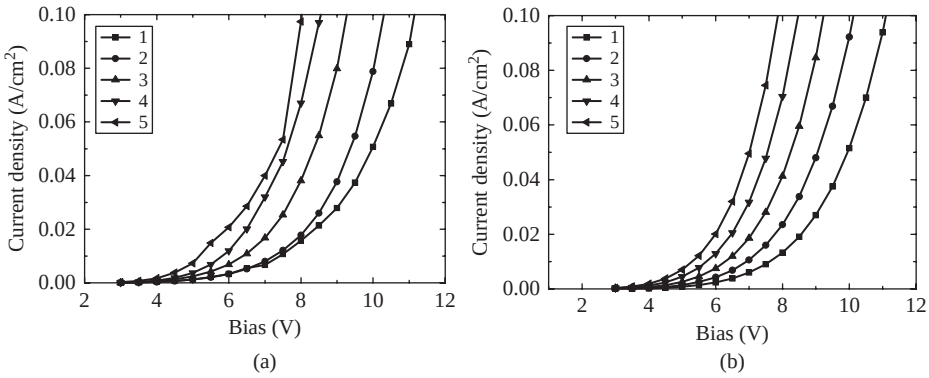


Figure 7.33 (a) Experimental and (b) simulated J - V characteristics of devices 1 to 5.

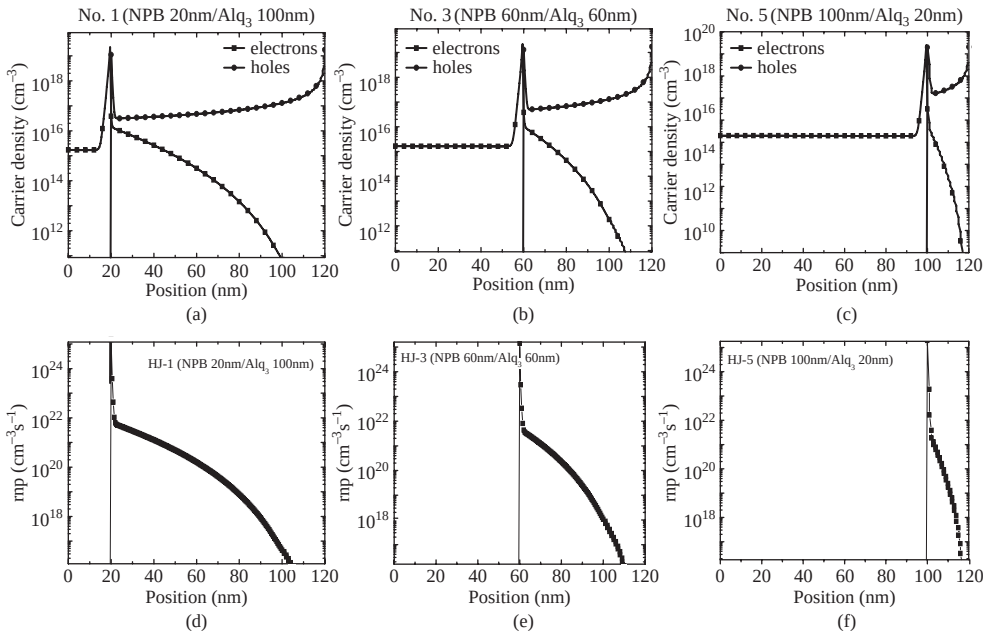


Figure 7.34 Simulated results of (a–c) carrier density and (d–f) recombination rate distributions of devices 1, 3 and 5.

Figure 7.35(a) shows the luminance versus current density for devices 1 to 5. We can see that the luminance increases then decreases as the HTL thickness increases. As shown in Figure 7.34, maximum recombination occurs at the HTL–ETL interface. To have constructive wide-angle interference, the recombination position must be located at $\lambda/4n$ from the reflective cathode, derived from Equation (7.39). Considering the peak wavelength of PL emission at 530 nm and that the refractive index of the organic material is about 1.6, the $\lambda/4n$ value is about 82 nm, which means device 2 should be close to the optimization condition of the constructive wide-angle interference. Experimental spectra of the devices are shown in Figure 7.35(b). The EL emission spectral peaks are at 558, 544, 536, 534 and 526 nm for devices

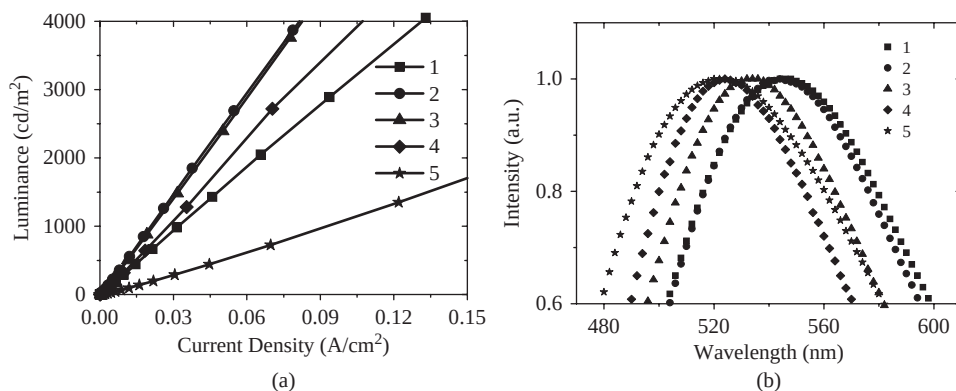


Figure 7.35 Measured (a) luminance versus current density and (b) EL spectra of devices 1 to 5.

1 to 5. Such a blue shift can be understood from the wide-angle interference. Since the interference is wavelength dependent, the enhancement ratio blue-shifts on increasing the recombination zone towards the cathode, i.e. increasing the HTL thicknesses.

7.5.5 Degradation mechanisms

Lifetime is one of the major obstacles to wide commercial applications for OLEDs. Although the operation principles of LEDs and OLEDs are similar, the lifetime of OLEDs is much shorter (typically less than a tenth) than that of LEDs. The main reasons are that (1) OLEDs have a thinner layer structure, (2) organic materials are sensitive to moisture and oxygen and (3) organic materials are not as robust as semiconductors due to larger vibration energy. Degradation in OLEDs can be categorized as three independent modes: (1) dark-spot formation, (2) catastrophic failure and (3) intrinsic degradation.

Dark-spot formation is the increase in nonemissive regions with time. This occurs even during OLED storage,⁸² and the growth rate may be accelerated by operation. The formation mechanisms of the dark spots are electrochemical reactions of the organic (or electrode) materials with environments. To slow down dark-spot formation, as described in Section 7.5.3.2, encapsulation or passivation is needed to prevent oxygen and moisture from attacking the OLED. There are many possible root causes which lead to the dark-spot phenomenon. Dark spot means nonemission at a certain area rather than luminance decrease in the whole emissive zone, which means structural defects in OLEDs produce the dark spot. The root causes of the structure defects include the following: (1) the layer between cathode and organic layers produces bubble structure which impedes electron injection and loses contact between the cathode and organic layer, which leads to a nonemissive zone;⁸³ (2) pinholes on the cathode provide a pathway for water and oxygen diffusion which oxidize the cathode metal and react with the organic materials;⁸⁴ and (3) intense decomposition of the ITO and organic film caused by local temperature rises releases volatile species which lead to local delamination and to oxidation of the cathode.⁸⁵ Figure 7.36 shows OLED images during operation taken under an optical microscope, just after device fabrication and after storage at 85 °C/100 % relative humidity for three hours. It is clear that the dark spots exist when the device is fabricated, and they grow with time.

Typically, control of substrate cleanliness and smoothness and device fabrication process reduces the density of structural defects, and the potential of dark spots is also reduced. Another way is using hermetic sealing of the OLED in an inert gas environment, which can control dark-spot degradation.⁸⁶ Heating the substrate between the organic evaporation⁸⁷ can also reduce the dark-spot area. But this can change some organic layer characteristic at the same time.

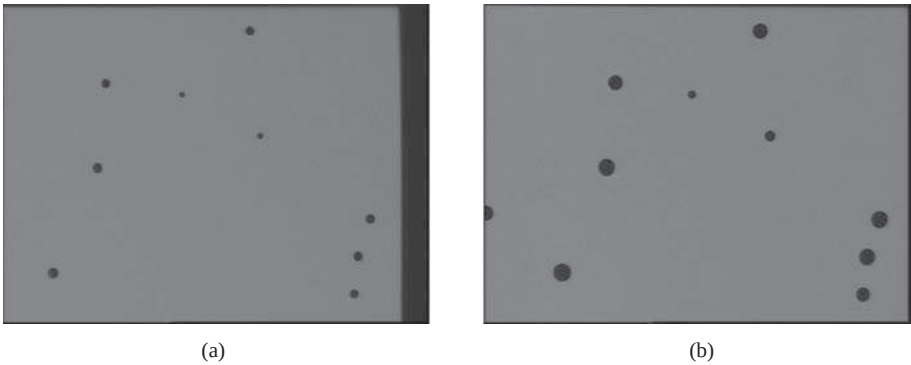


Figure 7.36 Images of EL from an OLED showing dark spots (a) when the device is just fabricated and (b) after storage at 85 °C/100 % relative humidity for 3 h.

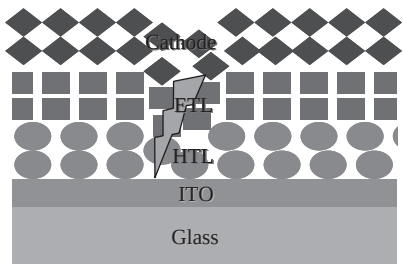


Figure 7.37 ITO spike in an OLED which results in catastrophic failure.

Catastrophic failure means a luminance decrease and huge current increase because of electrical shorts caused by defects in organic layers.⁸⁸ This also originates from morphological defects, such as ITO spikes. Since the organic layer thickness is only 100 nm, substantial roughness of ITO results in the topological change of the subsequent organic thin films. As shown in Figure 7.37, if there is an ITO spike, the organic thin films will be thinner there. When the device is operated under high electric field or after a long time, the progressive electric short phenomenon appears because of collapse of the defect position. To improve this, it is straightforward to maintain the morphology of the OLED. After device fabrication, it is also possible to burn out localized conduction filaments by applying a reverse bias.⁸⁹

Even though the morphology and encapsulation of an OLED are completely perfect, uniform luminance decay and driving voltage increase with time under constant current driving can still be observed, which is called intrinsic degradation. There are many reports on the mechanisms of OLED degradation. (1) Ions from the electrodes diffuse to the light-emitting zone: indium ions from the ITO anode and metal ions from the cathode (Mg:Ag or LiF/Al) will diffuse through into the EML.^{90, 91} They form fluorescence quenchers and decrease the luminance under a fixed driving current. Meanwhile, the mobile ions also create a built-in voltage that increases the driving voltage under the same electrical current. (2) Impurities that exist in the organic materials migrate in devices: Zou *et al.* reported that AC-driven devices may have longer lifetimes than those of DC-driven devices because the impurities may be drawn back in the reverse bias of the AC mode.⁹² (3) Decomposition of light-emitting materials: Cao *et al.* reported that the loss of conjugation of PPV was the main decay mechanism and reported that the intrinsic lifetime of PPV-based PLEDs was limited by the amount of charge flowing through the devices rather than AC or DC drive modes.⁹³ (4) Loss of contact of electrode–organic layers: this type of decay is not intrinsic and the device may be recovered by recoating the cathode.⁹⁴

Also, one of the major degradation mechanisms which may account for the long-term stability is the ‘unstable cation’ model. As mentioned in Section 7.5.2, the heterojunction in an OLED helps to confine the carriers which improves the current efficiency. However, at the same time, the carriers pile up at the HTL–EML interface. Since the injected holes from the HTL to the EML form cations in the EML material which are chemically unstable, this will accelerate the formation of nonradiative trapping centers and result in luminance decay and voltage increase of a device.⁹⁵

Popovic and Aziz designed an experiment to observe this degradation mechanism.⁹⁶ Figure 7.38 shows the PL intensity versus time of 5 nm thick Alq₃, sandwiched between two thick NPB and tetraphenyl-triazine (TPT) layers. NPB and TPT are the HTL and ETL materials, providing hole and electron transport through the Alq₃ thin layer under a bias. We can see that, after hole transport through the Alq₃ layer, a gradual decrease of the PL intensity is observed, revealing a continuous decrease in the PL intensity of the Alq₃ on prolonged current flow. The decrease in the PL intensity of the Alq₃ points to its degradation as a result of hole transport, thus revealing that cationic Alq₃ species are unstable and that their degradation products are fluorescence quenchers. On the other hand, while significant PL decrease is observed in the case of transporting holes into Alq₃, the PL stays remarkable constant in the case of transporting electrons. These results provide evidence that injection of holes into the Alq₃ layers of OLEDs is one of the main factors in device degradation.

When aging an OLED, not only does the luminance decay but also the voltage increases with constant driving current. Lee *et al.* have verified that a major degradation mechanism in an OLED is cation formation by conducting a series of experiments with the same organic materials and different device structures.⁹⁷ If the metal ion diffusion was the major degradation mechanism, a thicker HTL or ETL might result in longer lifetime. However, the operation lifetime of the thicker device was no better. On the other hand, the lifetime correlates with the power efficiency, as shown in Figure 7.39. As mentioned before, higher power efficiency means better energy transfer from electrical to optical power. Hence, the organic degradation comes from the chemical reaction which shows a higher reaction rate with higher temperature, i.e. lower power efficiency. With the same power efficiency, we can see the lifetime is longer with a thicker HTL, i.e. electron-rich device. A thicker HTL means the hole density is less near the recombination interface and there is less cation formation.

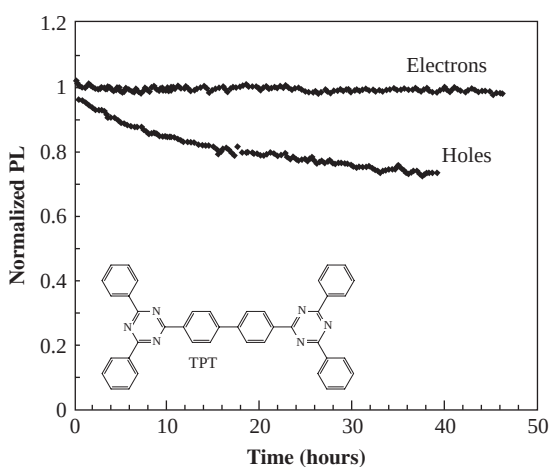


Figure 7.38 PL as a function of time for hole and electron only devices.⁹⁶ (Source: Popovic, Z.D. and Aziz, H., Reliability and degradation of small molecule-based organic light-emitting devices (OLEDs). *IEEE J. Sel. Top. Quantum Electron.*, **8**, 362. © 2002 IEEE)

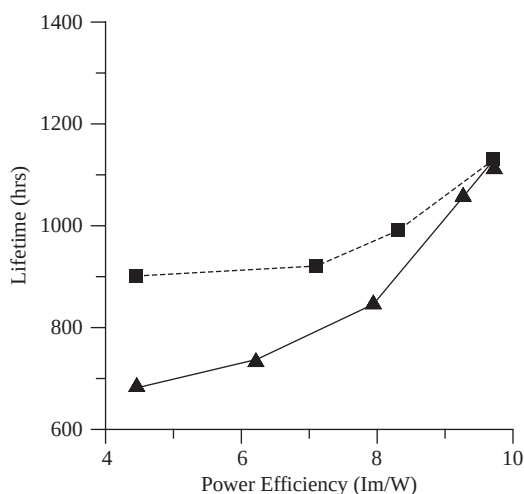


Figure 7.39 Dependence of lifetime on power efficiency. Dashed line and square symbols correspond to electron-rich devices. Solid line and triangular symbols correspond to hole-rich devices.⁹⁷ (Reprinted from Lee, J.H., Huang, J.J., Liao, C.C. *et al.*, Operation lifetimes of organic light-emitting devices with different layer structures. *Chem. Phys. Lett.*, **402**, 335. Copyright (2005), with permission from Elsevier)

A linear correlation was also found between the trap formation rate and the quencher formation rate at the HTL–ETL interface, as shown in Figure 7.40. Since voltage increase and luminance decay directly correlate to trap and nonradiative center formation, a linear relationship is found which means the thermally assisted chemical reaction induces organic material degradation near the recombination interface, which in turn quenches the photons and traps the carriers.

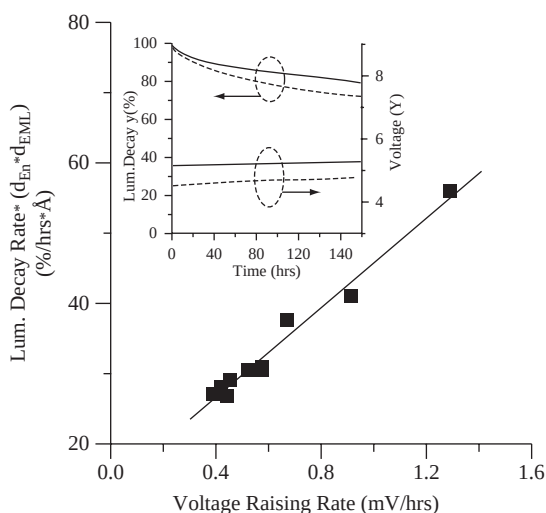


Figure 7.40 Voltage increase rate versus the luminance decay rate times the total thickness of EML and ETL. The inset shows typical curves of luminance decay and voltage as a function of time.⁹⁷ (Reprinted from Lee, J.H., Huang, J.J., Liao, C.C. *et al.*, Operation lifetimes of organic light-emitting devices with different layer structures. *Chem. Phys. Lett.*, **402**, 335. Copyright (2005), with permission from Elsevier)

Since the lifetime of an OLED is as long as 10 000 h under normal operation, some accelerating measurement and extrapolating methods are needed to estimate the lifetime value systematically in a shorter period.^{98, 99} However, acceleration might introduce other aging mechanisms, making the estimation of the lifetime a complex issue. Under high luminance aging, a typically used relation is

$$L_0^n t_{1/2} = \text{constant}, \tag{7.43}$$

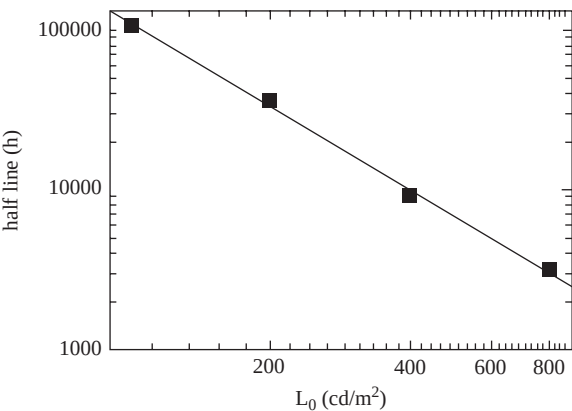


Figure 7.41 Half-life versus initial luminance on a double-logarithmic scale.¹⁰⁰ (Reprinted with permission from Féry, C., Racine, B., Vaufrey, D. *et al.*, Physical mechanism responsible for the stretched exponential decay behavior of aging organic light-emitting diodes. *Appl. Phys. Lett.*, **87**, 213502. Copyright (2005), American Institute of Physics)

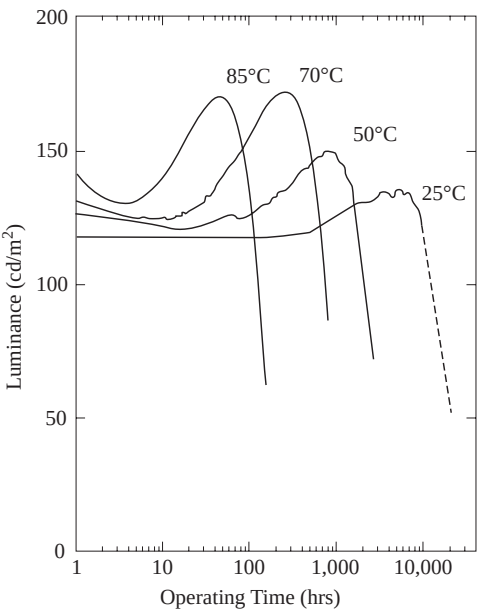


Figure 7.42 Luminance versus time for different environment temperatures on a semilogarithmic scale.¹⁰¹ (Reprinted with permission from Parker, I.D., Cao, Y. and Yang, C.Y., Lifetime and degradation effects in polymer light-emitting diodes. *J. Appl. Phys.*, **85**, 2441. Copyright (1999), American Institute of Physics)

where n is the acceleration coefficient and $t_{1/2}$ is the half-life. As shown in Figure 7.41, the best fit has been obtained with $n = 1.7$.¹⁰⁰ From Figure 7.41 we can see that the half-life is 40 000 h under 200 cd m^{-2} . If the luminance is increased to $10\,000 \text{ cd m}^{-2}$ for acceleration tests, we obtain a half-life of 51 h.

Another problem is that the luminance may not decrease monotonically, which means more than one mechanism may influence the OLED degradation during aging tests.¹⁰¹ This increases the complexity in analyzing the results. Figure 7.42 shows luminance versus time for different environment temperatures. We can see that the luminance remains constant, increases and then drops rapidly. There are three distinct mechanisms to account for the degradation behaviors. Also, with different temperatures, the lifetime performance changes.

7.6 Improvement of internal quantum efficiency

To improve the IQE, full utilization of triplet excitons is necessary which can increase the OLED luminance by a factor of four, as described in Section 7.3.2. By introducing a heavy metal into the organic materials, the spin–orbital coupling efficiency can be enhanced and strong phosphorescence due to the recombination from the triplet excited state is observed, which makes 100 % IQE possible. A tandem structure, which is series connection of several OLEDs, was proposed to increase the luminance and extend the operation lifetime. Since the OLEDs are stacked together, when one electron–hole pair is input through the external circuit, it appears as if more than one photon is emitted, which means the IQE of this system seems larger than 100%. Since the phosphorescent materials cannot cover the whole visible spectrum (especially the pure blue region), a combination of fluorescent and phosphorescent emitters is needed to harvest the excitons or to sensitize the triplet recombination, for achieving high IQE at the desired wavelength. These two methods are commonly used for broad-band OLEDs, such as white devices.

7.6.1 Phosphorescent OLEDs

Typically, phosphorescent emission is a slower and less efficient process than fluorescent emission since the decay of triplet states in conventional organic materials is generally not allowed due to the conservation of spin symmetry.¹⁰² This restricts the upper limit of the IQE of an OLED to 25 %, and 75 % of the energy from the triplet excited energy is wasted. However, by introducing a heavy metal atom in a molecule, the radiative decay of triplet dopant is possible. There are two mechanisms accounting for the EL emission from a phosphorescent dopant. The first is through energy transfer and the second is carrier trapping. As shown in Figure 7.43, there are two means of energy transfer in OLEDs. First, Förster energy transfer is a long-range process where donor (D) transfers to acceptor (A) by dipole–dipole coupling (Section 7.3.4.1). However, Förster transfer requires that the transition from excited state to ground state of both D and A must be allowed according to conservation of spin symmetry. Thus, this only transfers energy to the singlet state of the acceptor. In contrast, Dexter energy transfer, a short-range process, transfers energy by exchanging electrons of donor and acceptor. Unlike Förster energy transfer, Dexter energy transfer requires only the total spin to be conserved. It allows both singlet–singlet and triplet–triplet energy transfer. Also, direct trapping of carriers is important for the emission of phosphorescent OLEDs. Since the energy gap of a triplet dopant is usually smaller than that of the host, the triplet dopant may trap carriers and then lead to the direct formation of excitons at dopant sites.

As described above, with the strong spin–orbital coupling of heavy-metal complexes, phosphorescent materials can break up the spin-forbidden rule of non-radiative relaxation of the triplet state. Therefore, high-efficiency phosphorescent OLEDs can be realized. One of the most successful green phosphorescent material is fac-tris(2-phenylpyridine)iridium (Ir(ppy)_3) with 4,4'-N,N'-dicarbazolebiphenyl (CBP) as the host, which demonstrates peak current efficiency and power efficiency of 26 cd A^{-1} and 19 lm W^{-1} under a luminance of 100 cd m^{-2} .¹⁰³ Figure 7.44 shows the device structure and the organic structures.

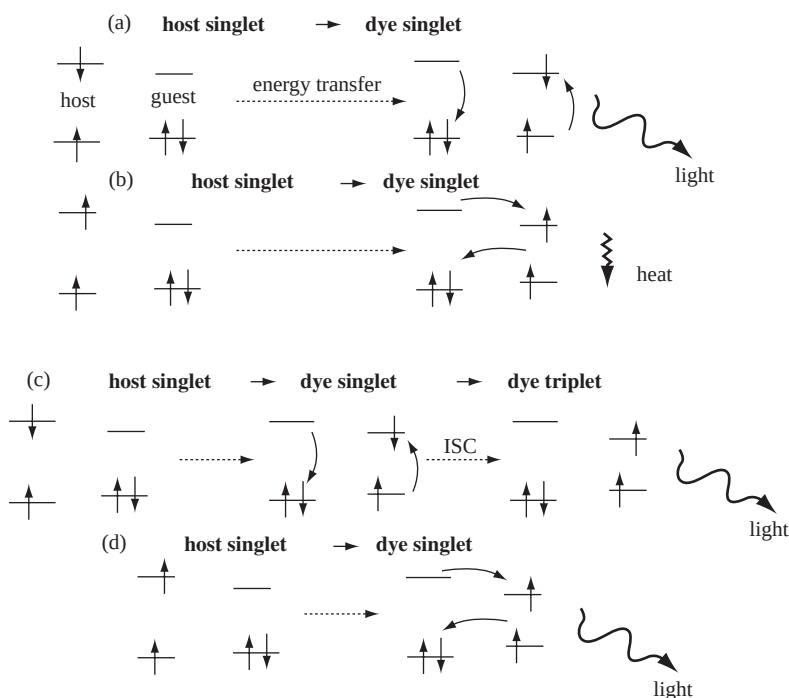


Figure 7.43 Energy transfer mechanisms in a guest–host system of an OLED: (a, b) energy transfer of the fluorescent dopant; (c, d) energy transfer of the phosphorescent dopant.¹⁰² (Reprinted with permission from Baldo, M.A., O’Brien, D.D., Thompson, M.E. and Forrest, S.R., Excitonic singlet-triplet ratio in a semiconducting organic film. *Phys. Rev. B*, **60**, 14422. Copyright (1999) by the American Physical Society)

Since CBP is a bipolar transport material, i.e. capable of transporting holes and electrons, one more layer, the HBL, is inserted to confine the excitons in the EML. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is widely used as a HBL due to its wide bandgap and large HOMO value, which can hinder the diffusion of excitons formed in the EML and prolong their residence time, thereby increasing the probability of energy transfer from the host to the phosphorescent dopant. However, the low glass transition temperature (T_g) of BCP (83 °C) may lead to device instability. Thus, an alternative, aluminum(III) bis(2-methyl-8-quinolinato)-4-phenylphenolate (BALq), with a higher T_g value can be used which shows higher stability.¹⁰⁴ By using a p–i–n structure to improve the injection of carriers, a green phosphorescent OLED with the highest power efficiency of 62 lm W⁻¹ and current efficiency of 61 cd A⁻¹ at 1000 cd m⁻² has been demonstrated.^{105, 106}

By using platinum(II) 2,3,7,8,12,13,17,18-octaethyl-12H,23H-porphine (PtOEP)¹⁰⁷ as a red dye, an OLED can be realized with an external quantum yield of 5.6 % using a CBP host.¹⁰⁸ However, due to the relatively long phosphorescent lifetime (~50 μs), use of PtOEP tends to lead to triplet–triplet annihilation at high current density. Several other red phosphorescent materials with shorter lifetimes have been proposed, such as bis(2-(20-benzo[4,5-a]thienyl)pyridinato-N,C30)iridium(acetylacetonate) (Btp2Ir(acac)) and Ir(3-piq)₂(acac).^{109–112} Due to the very short exciton lifetime of Ir(3-piq)₂(acac), 1.04 μs, it achieves the highest current efficiency of 23.94 cd A⁻¹ under a voltage of 8.29 V.¹¹² Considering the development of blue phosphorescent materials, there are difficulties in using energy transfer to excite deeper blue phosphorescent materials. With the increasing energy gap of phosphorescent dopant, a larger energy gap of the host is needed. Also, even with a suitable host, the larger energy gap of

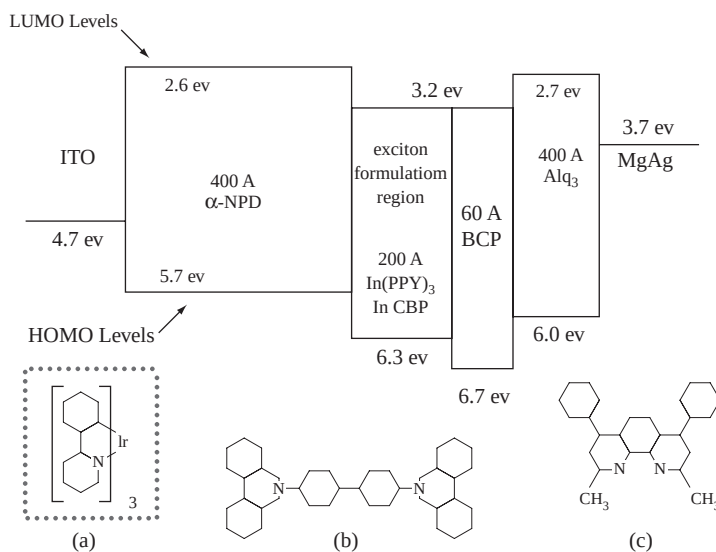


Figure 7.44 Device structure and chemical structures.¹⁰³ (Reprinted with permission from Baldo, M.A., Lamansky, S., Burrow, P.E. *et al.*, Very high-efficiency green organic light-emitting devices based on electrophosphorescence. *Appl. Phys. Lett.*, **75**, 4. Copyright (1999), American Institute of Physics)

phosphorescent dopant may result in difficulty for carrier injection. An efficient blue phosphorescent material is FIrpic which exhibits a current efficiency and power efficiency of 12 cd A^{-1} and 5 lm W^{-1} under 100 cd m^{-2} .¹¹³

7.6.2 Tandem structure

The operation principle of a tandem device is to inject one electron-hole pair into the EML to produce multiple electron-hole pairs through a charge generation layer (CGL) connected between each OLED unit, as shown in Figure 7.45.^{114, 115} The CGL can be composed of a metal thin film¹¹⁴ or a tunneling junction.^{116, 117} In a tandem device, current efficiency, in terms of cd A^{-1} , would scale linearly with the number of single OLED units, even more than unity. Due to the high current efficiency, a tandem device can achieve the same luminance at lower driving current and generate less heat, which in turn increases the operation lifetime.¹¹⁸ By connecting different color units, high-efficiency white OLEDs can be obtained. With suitable design of the layer structures, devices with high external quantum efficiency and high color purity can also be achieved.

One of the key factors in a tandem device is the design and the fabrication of the CGL which can be conductive or insulating thin films. First we discuss the conductive case. With a proper layout design, conductive CGLs can also be used as the contact pads of vertical stacking OLEDs that emit three primary colors, as shown in Figure 7.46. In this case, each OLED unit can be driven independently and can be used for fabricating a full-color display with high aperture ratio, named a stacked OLED (SOLED).^{119, 120} Typically, high work function materials, like ITO, gold and nickel, are used as the anode of an OLED device for effectively injecting holes into the p-type organic materials. In contrast, low work function materials, like alkali metals and alkaline earth metals, are good candidates for cathode materials.¹³ However, in a tandem OLED, a common metal CGL is necessary which can inject holes and electrons from the anode and cathode to the p- and n-type organic materials, respectively. Techniques for

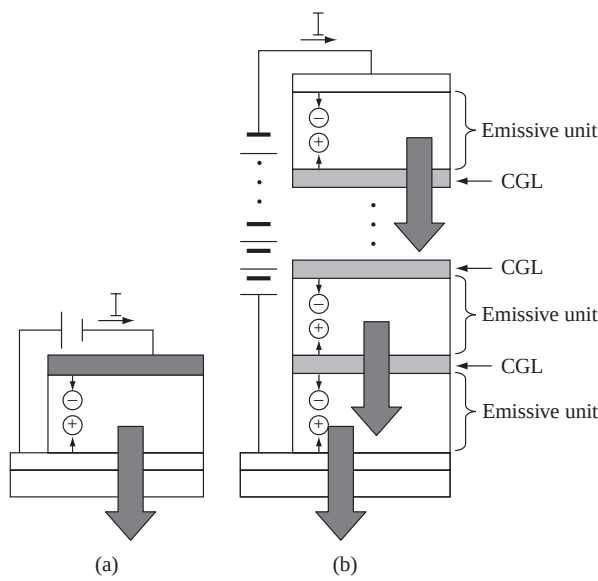


Figure 7.45 Structures of (a) a conventional OLED and (b) a tandem device.¹¹⁴ (Source: Matsumoto, T., Nakada, T., Endo, J. *et al.* (2003) Multiphoton organic EL device having charge generation layer. *SID Digest*, 979. Reproduced by permission of SID)

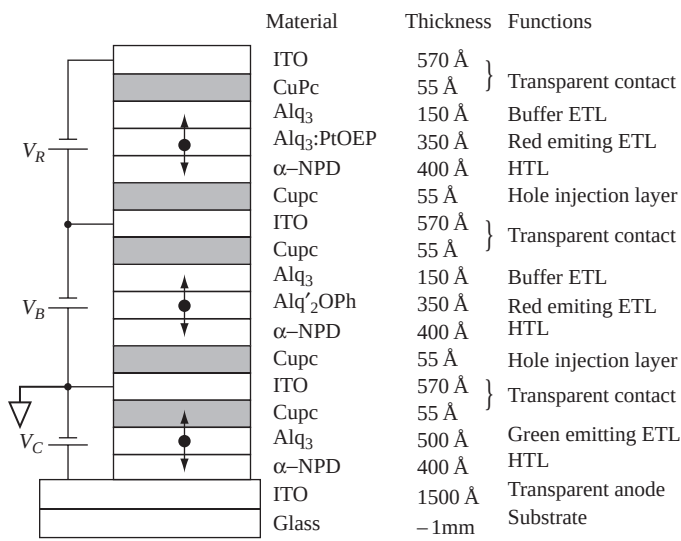


Figure 7.46 Schematic cross-section with conductive CGLs.¹¹⁹ (Reprinted with permission from Gu, G. *et al.*, Transparent stacked organic light emitting devices: I. Design principles and transparent compound electrodes. *J. Appl. Phys.*, **86**, 4067. Copyright (1999), American Institute of Physics)

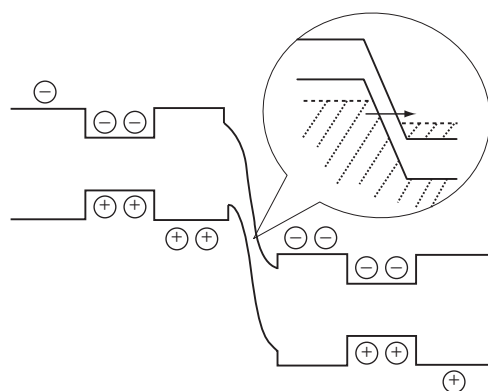


Figure 7.47 Energy band diagram of a tandem semiconductor LED with magnified reverse biased tunneling junction band energy diagram.¹¹⁸ (Reprinted with permission from Guo, X. *et al.*, Thermal property of tunnel-regenerated multiactive-region light-emitting diodes. *Appl. Phys. Lett.*, **82**, 4417. Copyright (2003), American Institute of Physics)

fabricating transparent or top-emitting OLEDs can be used here as the conductive CGL in a tandem device.

The concept of the insulating CGL, using a tunneling junction, is illustrated as follows. A reverse biased tunneling n–p junction is sandwiched between two OLED units. After an electron–hole pair is recombined in the previous OLED unit, the electrons in the p-side HOMO will tunnel into the n-side LUMO which can generate radiative recombination again in the next unit. Such a technique is widely used in semiconductor LEDs and laser diodes (LDs) to increase IQE, improve thermal stability and decrease threshold current of a LD, as shown in Figure 7.47.^{121, 122} In semiconductor devices, such a tunneling junction is fabricated with n- and p-type materials of high carrier concentration by controlling the doping ratio during semiconductor epitaxy. However, intrinsic organic materials usually have large bandgaps, i.e. 2 to 3 eV. Therefore the intrinsic concentration of thermally generated free carriers is generally negligible, i.e. less than 10^{10} cm^{-3} .²³ Similar to semiconductor materials, impurities are doped into the organic materials that can either transfer an electron to the LUMO states (n-type doping) or remove an electron from the HOMO states (p-type doping) to generate a free electron or hole (Section 7.5.1.3).

7.6.3 White OLEDs

For lighting applications, fluorescent lamps have been used for decades. However, the mercury in fluorescent lamps leads to serious environmental pollution. Therefore, a nonpolluting and high-efficiency lighting technology, such as LEDs or OLEDs, is required.¹²³ Also, these two technologies can serve as planar backlights of LCDs. Although semiconductor LEDs have the advantages of high color purity and long lifetime, the problem of differential aging among LEDs in an array causes serious nonuniformity problems, especially for a large panel.

White light emission from an OLED can be realized by mixture of two complementary colors or three primary colors. The former method has the advantages of simpler structure. However, it results in the color shifting with various driving voltages and low efficiency compared to monochromatic OLEDs.^{124, 125} The color-shifting phenomenon results from recombination zone shifting, contributing to field-dependent carrier mobilities. Recently, color stability has been achieved by evaporating a mixed-solution target containing a blue host (BANE) and red dopant (DCM2) as the EML.¹²⁶ The proposed structure is shown

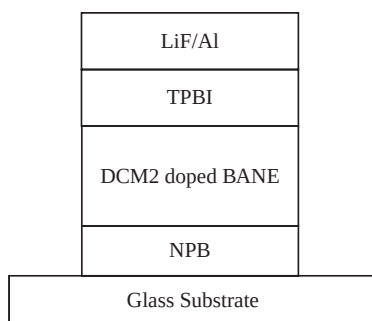


Figure 7.48 Structure using a mixture of three colors in the same EML.¹²⁶ (Reprinted from Jou, J.-H. *et al.*, Efficient, color-stable fluorescent white organic light-emitting diodes with an effective exciton-confining device architecture. *Org. Electron.*, **7**, 8. Copyright (2006), with permission from Elsevier)

in Figure 7.48. The best power efficiency is 6.5 lm W^{-1} (9.6 cd A^{-1}) at 12 cd m^{-2} with CIE coordinates of (0.346, 0.343). All color variations are less than (0.007, 0.006) between 100 and $10\,000 \text{ cd m}^{-2}$.

White OLEDs with tandem structures, which are several OLED components in series, have been proved to be able to enhance the efficiency,¹²⁷ as illustrated in Figure 7.49. The efficiency, 22 cd A^{-1} , of the tandem structure of two stacked components is more than double the efficiency, 8 cd A^{-1} , of the single device. This amplification comes from not only the nature of tandem structure (one electron-hole pair can generate more than one photon), but also the microcavity effect. However, it suffers from less color purity and spectrum shifting at various view angles.

Another concept, different from that mentioned above, of utilizing both singlet and triplet excitons provides dramatically high efficiency at high luminescence and eases the color-shifting problem at various injection current densities simultaneously.¹²⁸ The principle of management of singlet and triplet

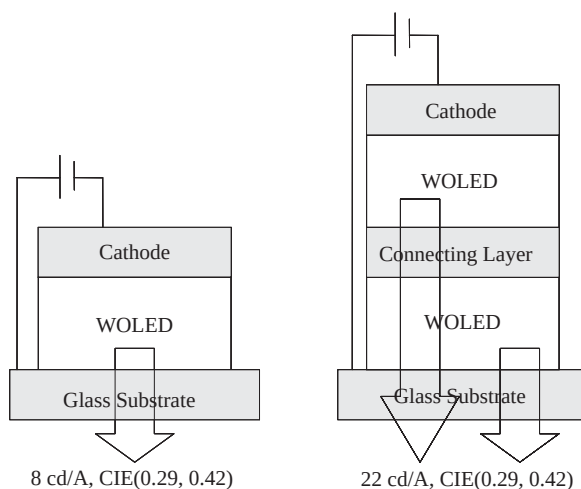


Figure 7.49 Architectures of white OLEDs in single (left) and tandem (right) devices, and their corresponding efficiencies and CIE coordinates.¹²⁷ (WOLED = white OLED.) (Reprinted with permission from Chang, C.-C., Chen, J.-F., Hwang, S.-W. and Chen, C.H., Highly efficient white organic electroluminescent devices based on tandem architecture. *Appl. Phys. Lett.*, **87**, 253501. Copyright (2005), American Institute of Physics)

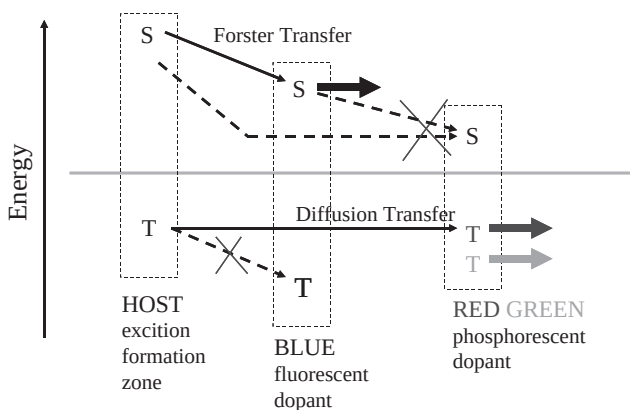


Figure 7.50 Energy transfer for exciton harvesting white OLED, which utilizes both singlet and triplet excitons.¹²⁸ (Reprinted by permission from Macmillan Publishers Ltd: *Nature* **440**, 908, Y. Sun *et al.*, Management of singlet and triplet excitons for efficient white organic light-emitting devices. Copyright (2006))

excitations is illustrated in Figure 7.50. First, excitons are generated in the host molecules. Second, singlet excitons are sequentially transferred to blue fluorescent dopants and triplet excitons to red and green phosphorescent dopants.

In order to implement this management, fluorescent dopants must be placed in the recombination zone and phosphorescent dopants must be appropriately doped slightly away from the recombination zone. This method not only eases the sharp roll-off behavior of efficiency due to triplet–triplet annihilation, but also reduces the color-shifting problem. Consequently, even at higher luminance, $\sim 500 \text{ cd m}^{-2}$, the external quantum efficiency and power efficiency remain high at 18.4 % and 23.8 lm W^{-1} .

To reduce manufacturing costs, the solution process is more suitable than vacuum deposition. A highly efficient white OLED with a combination of a solution-processed phosphorescent blue OLED with an appropriate down-conversion phosphor system has been demonstrated.¹²⁹ Blue light generated in the blend layer excites the OSRAM phosphors coated on the other side of a glass substrate. This system has a power efficiency of 25 lm W^{-1} , current efficiency of 39 cd A^{-1} and CIE coordinate of (0.26, 0.40). This highly efficient solution-based white OLED provides a cheaper manufacture for potential mass production.

7.7 Improvement of extraction efficiency

Typically, the external quantum efficiency (EQE), η_{ex} , of an OLED is related to the IQE, η_{in} , and the light extraction efficiency, η_{ext} , as¹³⁰

$$\eta_{\text{ex}} = \eta_{\text{in}} \eta_{\text{ext}}, \quad (7.44)$$

where η_{in} is the product of the fluorescent quantum efficiency of light-emitting material η_{F} , the fraction of recombinations that result in singlet excitons χ and the fraction of carriers recombined in the EML η_{re} .¹³¹

$$\eta_{\text{in}} = \eta_{\text{F}} \chi \eta_{\text{re}}. \quad (7.45)$$

For the commonly used ETL material Alq_3 , η_{F} is only about 30 %. It can be improved to nearly 100 % by introducing high-efficiency dopant materials into such a matrix. From spin statistics, EL from an OLED exhibits a value of χ of 1/4 for typically fluorescent materials. Values of η_{re} of nearly 100 % can be achieved under charge-balance condition by adjusting the thicknesses of the organic layers. From the above discussions, we can see that the upper limit of the η_{in} value is only about 25 %.¹³²

However, it is found that the maximum η_{ext} is only about 26.4 % even when the device structure is optimized. Most of the emitted light is confined within the OLED device due to the total internal reflection (TIR) at the interface between glass substrate and air, and waveguide effects of high refractive index organic layers.¹³³ Below are discussed the methods to improve the extraction efficiency.

1. *Eliminate the ITO/organic waveguide phenomenon.* Trapping of light in a medium is called the waveguide phenomenon, for instance the high-index guided (ITO/organic) mode. The easiest way to alleviate this effect is to reduce the thickness of those layers (e.g. ITO and organic layers); however, this is not practical.

Gu *et al.* used a shaped substrate (ITO) to redirect the edge light to the normal direction, which increases EQE by a factor of 1.9 ± 0.2 over similar OLEDs fabricated with flat glass substrates.¹³⁴ Yahiro and Tsutsui formed an extremely low refractive index silica aerogel layer ($n = 1.03$) between ITO and glass substrate, demonstrating an 80 % improvement.¹³⁵ Peng *et al.* inserted anodic aluminum oxide (AAO) nanoporous films between ITO transparent electrode and glass substrate and reported successfully extracting light from glass substrate with an apparent improvement (50 %).¹³⁶ Lee *et al.* introduced a two-dimensional photonic crystal (PC) pattern into the glass substrate of an OLED.¹³⁷ An increase in the extraction efficiency of over 50 % was successfully achieved because the periodic modulation converts the guided waves into external leaky waves. Matterson *et al.* demonstrated that Bragg scattering induced by a corrugated substrate can be used to increase the efficiency and control the spectrum and polarization of light from a polymer OLED.¹³⁸

2. *Avoid TIR at the interface of air and substrate.* Increasing the surface roughness of the substrate could help the substrate mode to be coupled out. Yamasaki *et al.* fabricated an OLED with a structure consisting of scattering medium and monolayer of silica microspheres to couple out the waveguide mode of light in the thin-film emissive devices.¹³⁹ Shiang and Duggal have given a more detailed discussion about the design of the scattering medium.¹⁴⁰ They mixed the different concentrations of high refractive index ZrO_2 ($d = 0.6 \text{ nm}$) into polydimethylsilicon resin (PDMS, $n = 1.42$) to get a maximum enhancement of 40 %.

Microlens-array films (MAFs) can be used to reduce the incident angle and avoid TIR to increase the external mode. Madigan *et al.* used microlenses, spherically shaped patterns, on the back of the device substrate. The emission intensity of OLEDs at normal viewing angle and the total external emission efficiency η_{ext} have been increased by factors of 9.6 and 3.0, respectively.¹⁴¹ However, Möller and Forrest discovered that attached microstructures may also result in image blur,¹⁴² and Lin *et al.* used a micropyramid for brightness enhancing applications.¹⁴³

Homework problems

- 7.1 Is it possible to fabricate a single-layer OLED? Why? If it is possible, what are the criteria for the organic material and the electrodes?
- 7.2 Assume there is a system with one host and two guest materials. One guest gives singlet blue emission, and the other triplet yellow emission. Sketch the possible energy transfer and the restrictions from the host to the guests to achieve 100 % IQE.
- 7.3 Derive the approximate SCLC equation as follows:
 SCLC: $J = \mu \varepsilon (V^2/L^3)$; where J is the current density, μ the carrier mobility, ε the static dielectric constant, V the driving voltage and L the device thickness.
 Current conduction: $J = \rho v$; where ρ is the injected free charge concentration and v the drift velocity.
 Capacitance: $Q = CV$; where Q is the total injected free charge and C the capacitance. (You may need $Q = \rho AL$, $v = \mu(V/L)$, A = device cross-section.)

(continued)

7.4 Derive the approximate TCLC equation as follows:

TCLC: $J = \varepsilon \mu N_c (\varepsilon / \varepsilon_0 N_0 k T_i)^l (V^{(l+1)} / L^{(2l+1)})$; where J is the current density, μ the carrier mobility, ε the static dielectric constant, V the driving voltage, L the device thickness and $l = T_i / T$. (Assuming the free and trap carrier concentrations are defined as follows. Free carrier concentration distribution: $n = N_c \exp[(F - E_c)/kT]$; trap carrier concentration distribution: $n_t = kT_i N_0 \exp[(F - E_c)/kT_i]$; N_c : effective density of states in the conduction band; F : quasi Fermi level; E_c : bottom edge of the conduction band energy; k : Boltzmann constant; T : temperature in kelvin; T_i : characteristic temperature.)

Current conduction: $J = \rho v$; where ρ is the injected free charge concentration and v the drift velocity.

Capacitance: $Q = CV$; where Q is the total injected free charge and C the capacitance. (You may need $Qt = \rho_i AL$, $v = \mu(V/L)$, $n = \rho/\varepsilon$, $n_t = \rho_i/\varepsilon$, A = device cross-sectional area.)

7.5 For a planar structure, does a top- or bottom-emission OLED exhibit higher EQE? Why?

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