

SOLAR CELL DEVICE PHYSICS

Second Edition

Stephen J. Fonash



Solar Energy/Physics

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SOLAR CELL DEVICE PHYSICS

Second Edition

Stephen J. Fonash

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This landmark new edition of Dr. Stephen Fonash's definitive work on solar cell physics has been updated to cover the major advances of the last two decades, including excitonic cells and nano-scale structures.

The book's authoritative semiconductor device-physics coverage has been augmented with in-depth consideration of the impact of nanomaterials and quantum confinement phenomena on photovoltaics. New topics incorporated into the text include nanostructures for light management and charge collection, plasmonics, multi-exciton production, and carrier multiplication.

Physical principles of solar cell operation are demonstrated with numerous simulations using the well known AMPS computer code. These provide readers with a visceral 'feel' for the inner workings of solar cell devices.

A sound fundamental basis for exploring the burgeoning field of photovoltaics, this pivotal resource provides rich coverage of the materials, structures, and underlying physics of photovoltaic devices.

By studying its contents, researchers, students, and engineers will gain a more robust understanding of the physical principles behind solar cells, discover new avenues for improvement, and ultimately open the door for more widespread use of solar energy.

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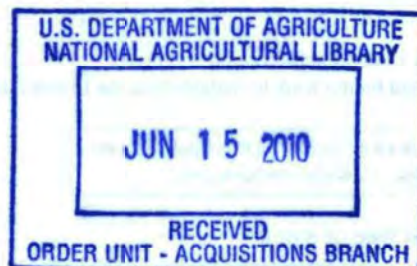
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Solar Cell Device Physics

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2.1 INTRODUCTION

In order to conceive new photovoltaic energy-conversion schemes, improve existing configurations, develop and improve cell materials, and understand the origins of the technical and economic problems of solar cells, the basics behind photovoltaic device operation must always be kept in the forefront. With that in mind, an overview of the material properties and physical principles underlying photovoltaic energy conversion is

presented in this chapter. The mathematical models for phenomena that are fundamental to solar cell operation, such as recombination, drift, and diffusion, are discussed rather than just presented. This is done with the firm conviction that awareness of the assumptions behind the various models better enables one to judge their appropriateness and to make adjustments as necessary, when analyzing and developing new solar cell structures. This is particularly the case for solar cells today, which can involve combinations of a variety of features or phenomena, such as nano-scale morphology, amorphous materials, organic materials, plasmonics, quantum confinement, and exciton-producing absorption.

2.2 MATERIAL PROPERTIES

Both solid and liquid materials are used in solar cells. Homojunction, heterojunction, metal-semiconductor, and some dye-sensitized solar cells use all-solid structures, whereas liquid-semiconductor and many dye-sensitized cells use solid-liquid structures. These materials can be inorganic or organic. The solids can be crystalline, polycrystalline, or amorphous. The liquids are usually electrolytes. The solids can be metals, semiconductors, insulators, and solid electrolytes.

2.2.1 Structure of solids

The solids used in photovoltaics can be broadly classified as crystalline, polycrystalline, or amorphous. Crystalline refers to single-crystal materials; polycrystalline refers to materials with crystallites (crystals or equivalently grains) separated by disordered regions (grain boundaries); and amorphous refers to materials that completely lack long-range order.

2.2.1.1 CRYSTALLINE AND POLYCRYSTALLINE SOLIDS

The distinguishing feature of crystalline and polycrystalline solids is the presence of long-range order, represented by a mathematical construct termed the lattice, and a basic building block (the unit cell), which, when repeated, defines the structure of the lattice. The atoms or molecules of the crystal have their positions fixed with respect to the points of the lattice. Amazingly, there are only 14 crystal lattices possible in a three-dimensional universe.¹ Four common ones are shown in Figure 2.1. Different planes in a crystal can have different numbers of atoms residing

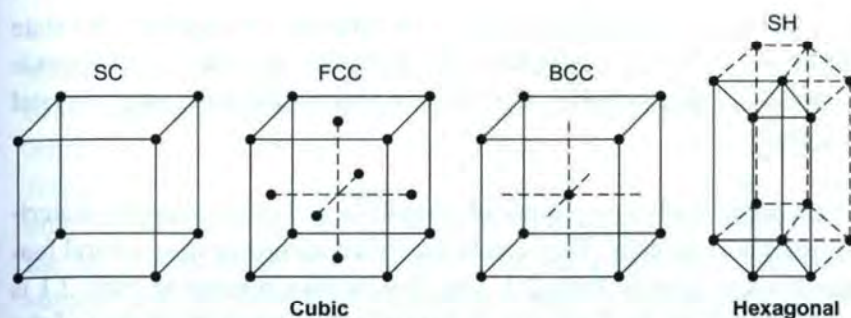


FIGURE 2.1 Some important unit cells characterizing crystalline solids. The simple cubic (SC) unit cell has lattice points only at the cube corners, the face-centered cubic (FCC) unit cell has additional lattice points in the center of each cube face, whereas the body-centered cubic (BCC) unit cell has lattice points at the cube corners and an additional lattice point at the center of the cube. The simple hexagonal (SH) unit cell has lattice points at the corners defining each hexagonal face and at the center of these two faces.

on them, as may be deduced by comparing, for example, the simple cubic and the body-centered cubic lattices in Figure 2.1. In solids that are compounds (e.g., the semiconductors CdS or CdTe), different planes can even be composed of different atomic species. Miller indices are a convenient convention for labeling different planes.¹

Polycrystalline solids differ from single-crystal solids in that they are composed of many single-crystal regions. These single-crystal regions (grains) exhibit long-range order. The various grains comprising a polycrystalline solid may or may not have their lattices randomly oriented with respect to one another. If there is correlation in the orientations of the grains, the material is referred to as being an oriented polycrystalline solid. The transition regions in a polycrystalline solid that exist between the various single crystals are what we termed grain boundaries. These regions of structural and bonding defects can extend for perhaps a fraction of a nanometer or more and may even contain voids. Grain boundaries can have a significant influence on physical properties. For example, they can getter dopants or other impurities, store charge in localized states arising from bonding defects, and, through the stored charge, give rise to electrostatic potential energy barriers that impede transport.² The grain boundaries of polycrystalline materials can be broadly classified as either open or closed. An open boundary is easily accessible to gas molecules; a closed boundary is not. However, even

a closed boundary is expected to be an excellent conduit for solid-state diffusion. Diffusion coefficients are generally an order of magnitude larger along such boundaries than those observed in bulk, single-crystal material.²

There are actually many types of crystalline and polycrystalline materials used in solar cells. They can be classified according to structural feature sizes, as seen in Table 2.1. The classification scheme of Table 2.1 is used throughout this book. As is shown in the comments section of the table, there are large differences in the terminology currently in use.

Table 2.1 Some Material Structure Types

Material type	Size of single-crystal region	Comments
Nanoparticle	Particle size <100 nm. May be single crystal, polycrystalline, or amorphous.	Shapes include spherical and columnar-like. Quantum size effects possible for particles <10 nm. Semiconductor-type called quantum dots when size effects are present.
Nanocrystalline (nc) material	Made up of single-crystal grains each <100 nm.	Polycrystalline. In the case of Si, also called microcrystalline silicon ($\mu\text{c-Si}$). In the case of Si, nc-Si has small grains of crystalline silicon within an amorphous Si phase. Quantum size effects possible for grains <10 nm.
Microcrystalline (μc) material	Single-crystal grains <1000 μm to 100 nm.	Polycrystalline. Often simply called polycrystalline material.
Multicrystalline (mc) or semi-crystalline material	Single-crystal grains >1 mm.	Polycrystalline. Grains can be many cm or larger in size.
Single-crystal material	No grains nor grain boundaries.	Whole material is one crystal.

2.2.1.2 AMORPHOUS SOLIDS

Amorphous solids[†] are disordered materials that contain large numbers of structural and bonding defects. They possess no long-range structural order, which means there is no such thing as a unit cell and a lattice. Amorphous solids are composed of atoms or molecules that display only short-range order, at best. There is no necessity for uniqueness in the amorphous phase. For example, there are a myriad of amorphous silicon-hydrogen (a-Si:H) materials that vary according to Si defect density, hydrogen content, and hydrogen-bonding details.

Solids can also exist in a form that contains regions of crystalline and amorphous phases, as seen in Figure 2.2. The example used in the figure is a polymeric solid that has amorphous domains containing disordered polymer chains joined to crystalline regions where the chains form an ordered array. The existence of such mixed-phase solids, containing amorphous and micro-crystalline regions, often depends on the material fabrication procedure.

2.2.2 Phonon spectra of solids

Because of the interactions among its atoms, a solid has vibrational modes. The quantum of vibrational energy is termed the phonon. At a given temperature T , atoms of a solid are oscillating about their equilibrium sites; therefore, there are phonons present in the solid. In thermodynamic equilibrium, the distribution of phonons among allowed modes of vibration (phonon energy levels, E_{pn}) is dictated by Bose-Einstein statistics.

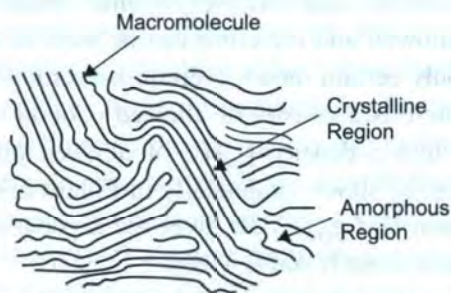


FIGURE 2.2 Organic solid containing crystalline and amorphous regions. Some of the polymer molecules constituting this solid are found in both regions.

[†]Glasses are a subset of amorphous materials which possess a glass transition temperature. Above this temperature glasses can flow.

Phonons can be involved in heat transfer, carrier generation (thermal or in conjunction with light absorption), carrier scattering, and carrier recombination processes. They behave like particles. For example, when an electron in a solid interacts with a vibrational mode, the event is best viewed as an interaction between two types of particles, electrons and phonons. Phonons have a dispersion relationship $E_{pn} = E_{pn}(\mathbf{k})$, which relates the phonon energy E_{pn} to the wave vector $\mathbf{k}$ [$|\mathbf{k}| = (2\pi/\lambda)$] of the vibrational mode. This is analogous to the dispersion relationship for light, which relates photon energy E_{pt} to the wave vector $\mathbf{k}$ of the light. For free space, this dispersion relationship for light has the extremely simple form $E_{pt} = \hbar c |\mathbf{k}|$ where $\hbar$ is Planck's constant divided by 2π . In the case of phonons, the function $E_{pn} = E_{pn}(\mathbf{k})$ is more complicated and gives what is termed the phonon spectrum or phonon energy bands in a solid. In the case of both phonons and photons, $\hbar \mathbf{k}$ has the interpretation of particle (phonon or photon) momentum.¹

2.2.2.1 SINGLE-CRYSTAL, MULTICRYSTALLINE, AND MICROCRYSTALLINE SOLIDS

In single-crystal, multicrystalline, and microcrystalline materials, both total energy and total momentum are conserved in phonon-electron interactions.¹ For example, in a "collision" between an electron and phonon in a crystal (or in a crystal region in the case of polycrystalline material), the change in the $\mathbf{k}$ -vector of the phonon and the electron must conserve total (electron plus phonon) momentum as well as energy. This constraint is termed the $\mathbf{k}$ -selection rule. In addition, in single-crystal, multicrystalline, and microcrystalline solids, only specified values of $\mathbf{k}$ are allowed and therefore can be used in the $E_{pn} = E_{pn}(\mathbf{k})$ relation.¹ Since only certain modes (certain $\mathbf{k}$ -vectors) are permitted in a given crystal, there is a density of allowed phonon states in $\mathbf{k}$ -space which translates into a density $g_{pn}(E)$ of allowed phonon states per energy per volume, as shown graphically in Figure 2.3. The density of states $g_{pn}(E)$ is such that $g_{pn}(E) dE$ gives the number of phonon states per volume between some E and $E + dE$.

The $\mathbf{k}$ -space just mentioned for plotting $E_{pn} = E_{pn}(\mathbf{k})$ in crystalline solids is also called reciprocal space. This space has a lattice, too, and its distances have the dimensions of reciprocal length. Directions in reciprocal space correspond to directions in the real crystal. The reciprocal-space lattice can be viewed as the Fourier transform of the real-space

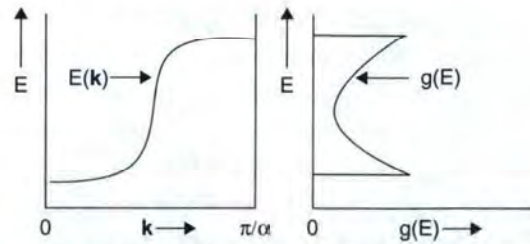


FIGURE 2.3 Relationship between the $\mathbf{k}$ values permitted to be used (not shown) in a dispersion function and the resulting density of states $g(E)$. This dispersion relation in $\mathbf{k}$ -space and its resulting density of states in energy may be that of phonons or electrons in a crystalline solid. It turns out that the density of states in energy $g(E)$ is the more basic concept than the allowed states in $\mathbf{k}$ -space, since it applies to noncrystalline materials, too; i.e., its validity does not depend on the existence of a $\mathbf{k}$ -space.

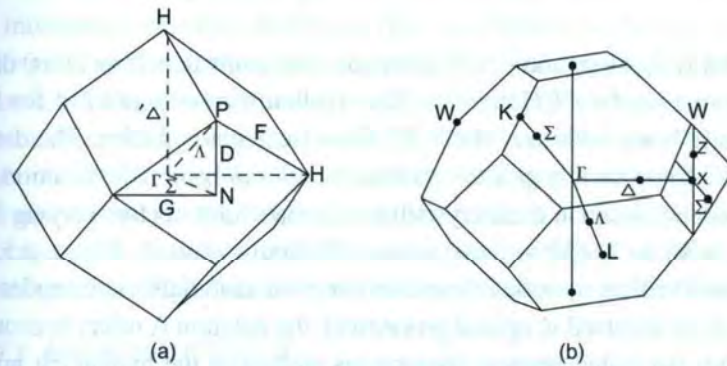


FIGURE 2.4 Brillouin zones for: (a) the BCC crystal lattice; (b) the FCC crystal lattice.

lattice of a crystal. Because the real-space lattice is so structured, its reciprocal-space lattice is equally structured. Just as all the information on the structure of a crystalline solid is contained in the unit cell of the real-space lattice, all the information on the dispersion relation $E_{pn} = E_{pn}(\mathbf{k})$ is contained in the unit cell of the reciprocal lattice. The unit cell in reciprocal space is termed the first Brillouin zone or simply the Brillouin zone.¹ The rest of reciprocal space repeats this $E_{pn} = E_{pn}(\mathbf{k})$ information. Figure 2.4 shows the Brillouin zones corresponding to the FCC and BCC real-space lattices seen in Figure 2.2. The notation is standard in Figure 2.4 and denotes symmetry points and axes.¹

A part of the phonon spectra $E_{pn} = E_{pn}(\mathbf{k})$ for two materials of interest to solar cell applications, crystalline silicon and gallium arsenide, is presented as an example in Figure 2.5. Here the function $E_{pn} = E_{pn}(\mathbf{k})$ is depicted for

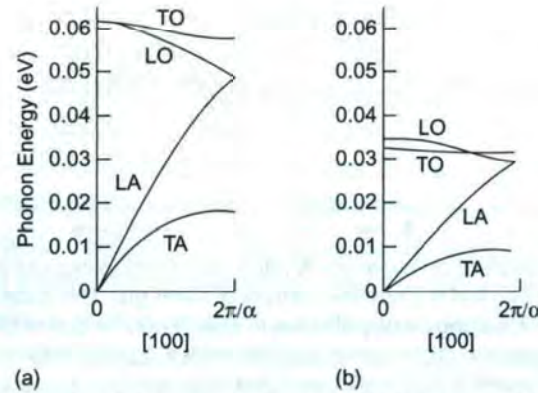


FIGURE 2.5 Phonon bands in two crystalline solids: (a) silicon, and (b) gallium arsenide. Phonon bands are depicted for $\mathbf{k}$ values lying along the Γ to X directions in the Brillouin zone of an FCC lattice. (From Ref. 3, with permission.)

$\mathbf{k}$ values lying along the Γ to X direction (and equivalent directions) of the Brillouin zone for FCC crystals. This Brillouin zone is utilized for both materials, since both have the FCC direct (real-space) lattice. The data in Figure 2.5 specifically give the phonon energies or bands (the functions are multivalued) found in these crystalline materials for $\mathbf{k}$ -vectors varying from Γ ($|\mathbf{k}| = 0$) to X ($|\mathbf{k}| = 2\pi/a$) in their Brillouin zone. In Figure 2.5, the notation O refers to optical branches (in polar materials these modes can be strongly involved in optical properties); the notation A refers to acoustic branches (so called because frequencies audible to the human ear are on these branches at about the origin in Fig. 2.5). The notations T and L refer to the transverse and longitudinal modes, respectively. The largest values of $|\mathbf{k}|$ in the Brillouin zone will depend on the lattice constant a of the semiconductor; however, using reasonable values of a , it is seen that $|\mathbf{k}|_{\max}$ in Figure 2.5 is of the order of 10^8 cm^{-1} . If we were to extend the ordinate and superimpose the plot for all photon energies $E_{\text{ph}} < 3 \text{ eV}$ (which easily covers the solar spectrum of Fig. 1.1) versus k onto Figure 2.5, we would see that such a plot would fall essentially on the ordinate. We can take a very important point from this: the momentum of the photons constituting the majority of the solar spectrum (see Fig. 1.1) is very small compared to the momentum of phonons. From Figure 2.5 it may also be inferred that phonon energies in solids are of the order of 10^{-2} eV to perhaps 10^{-1} eV . Photon energies, at least those in the near infrared, visible, and near ultraviolet range, where the spectra of Figure 1.1 are at their richest, are of the order of 1 eV .

2.2.2.2 NANOPARTICLES AND NANOCRYSTALLINE SOLIDS

As particle or grain size becomes smaller, the surface-to-volume ratio obviously increases and surface-stress effects on bulk and surface phonon modes become more important. However, when a nanoparticle's or nanocrystalline grain's characteristic dimension approaches some multiple ($<5\text{--}50$) of the lattice constant, very fundamental change is also possible; i.e., the vibrational modes can start to change, due to their being limited in spatial extent,^{4,5} and the constraint of a phonon energy corresponding to a well defined $\mathbf{k}$ -vector can disappear, also because of spatial limitations⁶—these changes are the result of what is termed phonon confinement. The removal of the constraint of a precise $\hbar\mathbf{k}$ for a phonon of a given energy makes sense if viewed in terms of Heisenberg's $\Delta x \Delta k = \theta(2\pi)^{\ddagger}$; i.e., as Δx becomes smaller due to confinement, the phonon momentum becomes ill-defined. The implication for phonon-electron “collisions” is that a phonon can now supply its energy and a range of momenta. As a particle becomes even smaller, the vibrational modes can become discrete in energy, as would be seen for a molecule. The impact of phonon confinement at a given nanoparticle or nanocrystalline grain size will depend on the degree to which isolation is accomplished. For nanocrystalline materials, this means that the proximity of other nanocrystal grains will act to reduce the influence of phonon confinement.

2.2.2.3 AMORPHOUS SOLIDS

In amorphous solids, a vibrational mode may extend over only a few nanometers. It therefore again follows from $\Delta x \Delta k = \theta(2\pi)$ that phonons in disordered materials are not characterized by a well-defined wave vector $\mathbf{k}$ and there is no phonon $\mathbf{k}$ -selection rule. The quantity $\mathbf{k}$ is no longer a “good quantum number.” In amorphous solids there is no Brillouin zone in reciprocal space because there is no unit cell in real space, since there is no crystal lattice. Also, in these materials, it becomes difficult to distinguish between acoustic and optical phonons. However, in amorphous solids, phonons play the same critical roles in electron transport, heat conduction, etc., as they do in crystalline solids.

It follows that the concept of density of $\mathbf{k}$ states in reciprocal space is not valid for amorphous materials. However, the concept of a density

[‡]The notation $\theta(2\pi)$ is being used to signify of the order of 2π .

of phonon states in energy $g_{pn}(E)$ is still valid. In fact, the $g_{pn}(E)$ of an amorphous solid will conform to that of the corresponding crystalline material to a degree depending on the importance of second nearest-neighbor, third nearest-neighbor, etc., forces.

2.2.3 Electron energy levels in solids

A very helpful approach that is usually valid for many solids is the Born-Oppenheimer or adiabatic principle. This principle asserts that, if one is solving the Schrödinger equation for the collection of the cores (nucleus plus core electrons) and valence electrons that make up a crystalline, polycrystalline, nanocrystalline, or amorphous solid, then one can separate the core motion (the vibration field we just discussed) from that of the valence electron motion.⁷ In this picture, a single electron “sees” an effective potential resulting from (1) the cores in their average positions and from (2) all the other valence electrons. Solving this single-electron problem gives rise to what are termed single-electron energy levels. However, as we note in this section, it is not always possible to separate the Schrödinger equation for a solid into one problem dealing with phonons and into another dealing with electrons treated as single particles immersed in an effective potential. For example, the multi-particle core-electron interactions in which the cores polarize to shield an electron’s charge give rise to multi-particle solutions to the overall Schrödinger equation which are called polarons. Multi-particle electron–electron interactions can give rise to solutions termed excitons. Polarons and excitons are examples of multi-particle states.

2.2.3.1 SINGLE-CRYSTAL, MULTICRYSTALLINE, AND MICROCRYSTALLINE SOLIDS

(a) Single-electron states

Because the unit cell of the direct lattice of a single-crystal, multicrystalline, and microcrystalline material completely specifies the structure, it completely determines the environment of an electron in a crystalline solid. Essentially, the Schrödinger equation for single-electron states in a crystal need be solved for only one unit cell, subject to boundary conditions that represent the periodicity of the structure. The dispersion relation $E = E(\mathbf{k})$ that comes out of this solution specifies the energy E available to an electron in a single-particle state with wave vector $\mathbf{k}$. This wave vector $\mathbf{k}$, when multiplied by $\hbar$, may be viewed as the

momentum of the electron, just as a phonon of wave vector $\mathbf{k}$ could be viewed as having the momentum $\hbar\mathbf{k}$ in a crystalline material. As in the case of the phonon dispersion relation for a crystal, the periodicity of the direct lattice ensures that the electron dispersion relation $E = E(\mathbf{k})$ is periodic in reciprocal space. Hence, all the $E = E(\mathbf{k})$ information is completely contained in the first Brillouin zone appropriate to the crystal. That information just repeats throughout the rest of $\mathbf{k}$ -space. As is also the case for phonons, only certain $\mathbf{k}$ -vectors in $\mathbf{k}$ - (reciprocal) space are permitted to electrons in a crystal. Consequently, there is a density of allowed electron states in $\mathbf{k}$ -space. Through the dispersion relationship, this can be transformed into a density of states in energy per energy per volume.¹ We designate this density of allowed electron single-particle states per energy per volume as the quantity $g_e(E)$. This is another example of the density of states in energy concept seen in Figure 2.3.

The $E = E(\mathbf{k})$ relationships between a single-electron allowed energy level E and the wave vector $\mathbf{k}$ for silicon and gallium arsenide are seen in Figure 2.6 for specified directions in the Brillouin zone. Both materials

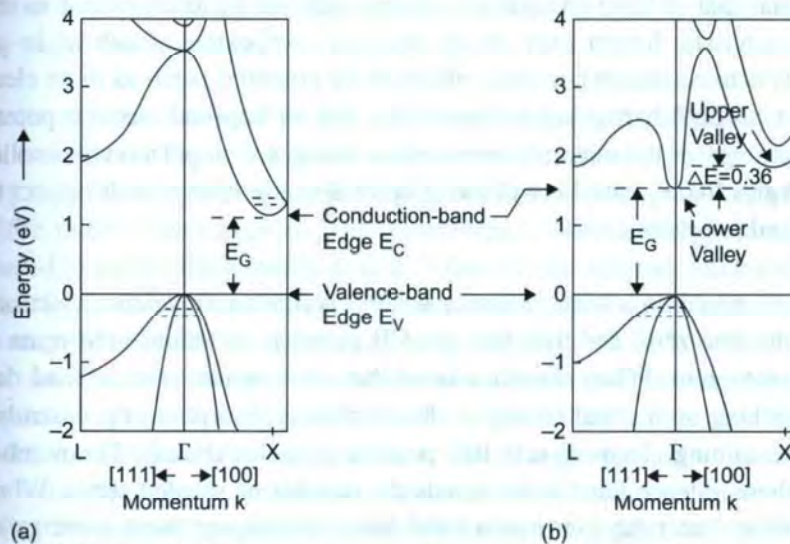


FIGURE 2.6 Allowed electron energies versus $\mathbf{k}$ -vectors (wave vectors) for two crystalline, inorganic semiconductors: (a) silicon; (b) gallium arsenide. Silicon is indirect gap (the maximum in the valence band E_V and the minimum in the conduction band E_C have different $\mathbf{k}$ -values); gallium arsenide is direct gap (the maximum in the valence band E_V and the minimum in the conduction band E_C have the same $\mathbf{k}$ -value). The valence band edges are aligned here in energy for convenience only. (After Ref. 3, with permission.)

have the same Brillouin zone, as noted in conjunction with the phonon plots of Figure 2.5. From the electron energy dispersion relationships for these two example materials, it can be seen that both have a lower band of allowed electron energy levels (actually two bands), then a gap of forbidden energies of width E_G , and finally a band (or, more precisely, overlapping bands) of allowed energy levels. This type of band structure—with allowed levels in a band, an energy gap with no allowed states, and then allowed levels in a band—typifies an ideal crystalline semiconductor, with the stipulation that the valence electrons completely fill that lower band at $T = 0\text{ K}$. In other words, this lower band is the home of all the valence electrons; consequently, it is called the valence band (VB). The highest allowed energy in this lower grouping of bands (valence band) is termed the valence band edge E_V . The lowest allowed energy in the upper grouping of bands (conduction band, CB) is termed the conduction band edge E_C . The energy levels in these bands are single-particle states that are delocalized; i.e., they extend throughout the crystal. Formally, bands like those seen in Figure 2.6 (which shows the locations in energy of E_C and E_V) are representative of a region in the crystal that is large compared to a unit cell but small compared to the characteristic length over which material composition (such as in an alloy semiconductor) or some electrostatic potential (such as in an electrostatic field barrier region) may vary. As an imposed electron potential energy or the material composition changes with position in a solid, energies like E_C and E_V will move up or down in energy with respect to a fixed reference.

As we noted, in a semiconductor the VB is filled with valence electrons at absolute zero, and therefore the CB is empty of valence electrons at absolute zero. When electrons leave the states of the valence band due to picking up thermal energy or due to photon absorption, the ensemble of remaining electrons acts like positive particles (holes). The number of these valence band holes equals the number of vacated states. When electrons enter the conduction band due to picking up thermal energy or due to photon absorption, they act like electrons and their number equals the number of electrons in that band.¹ The holes in the valence band are “free” carriers in that they are in delocalized states and can move in an electric field (drift) or diffuse. The electrons in the conduction band are “free” carriers in that they, too, are in delocalized states and can move

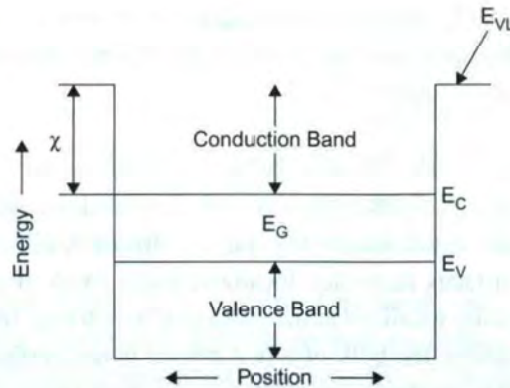


FIGURE 2.7 Schematic showing the energy bands available in a semiconductor as a function of position. Reference energy here is the vacuum energy E_{VL} .

in an electric field (drift) or diffuse. If essentially all the electrons per volume in the conduction band n came from the holes per volume p in the valence band, then the semiconductor is said to be intrinsic and $n = p$. If an intrinsic material is in thermodynamic equilibrium (TE), $n = p = n_i$ where n_i , the intrinsic carrier population in TE, is dictated by the energy gap and the temperature.³

Frequently, the detailed $E = E(\mathbf{k})$ information relating E and $\mathbf{k}$ shown in the examples of Figure 2.6 is not needed. In many applications it is necessary only to know the location in energy of the conduction band edge E_C , of the valence band edge E_V , and of the local vacuum level E_{VL} (energy needed to escape the material at x) as a function of position. Such a diagram is given, as a function of position x in the crystal and with respect to an arbitrarily chosen reference energy, in Figure 2.7. This diagram also introduces a new quantity, the electron affinity χ . This is the energy required to promote an electron from the bottom of the conduction band to the vacuum level at some position x . The energy required to go from the top of the valence band to the vacuum level at some position x is the hole affinity $E_G + \chi$, where E_G is the forbidden energy gap.

An ideal insulator differs from the ideal semiconductor of Figure 2.7 only in that $E_G \geq 2.5$ eV, where the lower bound of 2.5 eV is somewhat arbitrary. The real point is that, if a material is an insulator at room temperature, then its E_G is too wide to give any significant intrinsic carrier

population at 300 K. From the perspective of Figure 2.7 a metal arises either when the gap E_G is zero or when the valence electrons only partially fill the lowest band at $T = 0$.¹

Figure 2.7 represents the electron energy band scheme for a uniform composition, ideal crystal. Such a material only has the delocalized (extended) states of the valence and conduction bands. However, real materials have surfaces, and surfaces introduce localized states (with atomic-like wave functions physically localized at the surfaces), which may be populated by carriers.³ In addition, the bulk of a real crystal is not perfect, since in the bulk there will be impurities and defects that will also introduce localized, atomic-like states at the positions of the impurities and defects.³ Further, if a solid is nano-, multi- or microcrystalline, the structural and bonding defects that are the grain boundaries cause localized states to exist in the grain boundary regions. A localized state is represented in energy band diagrams like Figure 2.7 by introducing a short horizontal line drawn at its position in energy and space. Localized states may have energies that lie in the range of the bands or of the energy gap. The former case is uninteresting from a technological point of view because the levels are degenerate with those of delocalized band states. Consequently, carriers in such localized states immediately transfer to the delocalized states of the band and are free to move about. The latter case of states that lie in the energy gap is very important technologically because the carriers in these states cannot move—unless they are demoted or promoted to delocalized states. These states in the energy gap are often referred to as localized gap states or simply gap states. Drift and diffusion are not possible for carriers in gap states unless the gap state density is extremely high. Hopping transport, discussed shortly, can be possible for high densities. Gap states can be purposefully present to dope a material. Gap states can act as conduits between the conduction and valence bands (i.e., support generation and recombination) and they can store charge, thereby affecting the electric field in a device. If they principally do the latter but are not dopants, they are referred to as traps. As we discuss later, whether a gap state is principally a recombination center or a trap depends on its energy position and its capture cross-sections for electrons and holes.

Localized gap states found in crystalline, polycrystalline, amorphous, nanocrystalline, and nanoparticle solids may be broadly classified as

acceptor-like, donor-like, or amphoteric in nature. Acceptor and donor-like states are single-electron states with the following definitions³:

1. *Acceptor states* Neutral when unoccupied by an electron and, therefore, negative when occupied by an electron (ionized).
2. *Donor states* Neutral when occupied by an electron and, therefore, positive when unoccupied by an electron (ionized).

Amphoteric gap states can be occupied by none, one, or two valence electrons. Their charge state depends on their occupancy; e.g., one electron could be the neutral state, no electrons the positively charged state, and two electrons the negatively charged situation.

The charge per volume resulting from acceptor-like states at energy E in the gap depends on whether they have captured an electron and is given by $-en_T$ where n_T is the number of acceptor states per volume at the energy E that have been successful in capturing an electron. Correspondingly, the charge per volume resulting from donor-like states at energy E in the gap depends on whether they have lost an electron and is given by ep_T where p_T is the number of donor states per volume at energy E that have been successful in losing an electron. Amphoteric states, as noted, can give rise to positive or negative space charge, depending on their occupancy.

As mentioned, gap states can serve as sources (dopants) of carriers for the bands.³ They are purposefully introduced for this role (doping), when desired, or can be inadvertently present and have this function. Due to trapping and doping, the electrons in the conduction band per volume n and the holes in the valence band per volume p may not equal each other as they do in an intrinsic (i.e., defect-free) material. When this occurs, the material is referred to as extrinsic. Interestingly, it is possible to have so many gap states present in a material that they form a band within the energy gap. This is the high density of gap states situation mentioned earlier. These states, depending on the distance between the physical sources of the states, can be delocalized or localized in nature. Such a band within the energy gap is termed an intermediate band (IB).

(b) Excitons

Single-crystal, multicrystalline, and microcrystalline solids can also harbor the solutions to the Schrödinger equation that are known as polarons

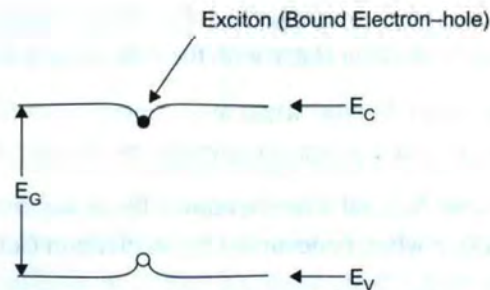


FIGURE 2.8 A representation of an exciton ground state superimposed on the single-electron levels of a band diagram.

and excitons. The former, an electron-phonon interaction as noted earlier, increases the inertia of electrons, thereby giving them a larger effective mass. Polarons are generally only of any significance in crystals with some degree of ionicity.¹ Excitons are of much more interest, since they are a multi-particle phenomenon that can be involved in the light absorption process in solar cell materials. Specifically, excitons are multi-electron solutions that may be viewed as an electron bound to a hole via Coulombic attraction.¹ Figure 2.8 shows an exciton ground state superimposed on the single-electron levels of a band diagram. The binding energy is the energy needed to have the exciton in its ground state dissociate into a free electron in the conduction band and a free hole in the valence band. Since the binding energy is dictated by the Coulombic attraction, materials that polarize more have lower binding energies; i.e., the binding energy correlates inversely with the dielectric constant. Excitons can be created by photon absorption and they can be mobile in a solid. When they move, energy, but not net charge, moves. Since they are not charged, they can only move by diffusion. The spatial extent of an exciton can be over several lattice constants (a Wannier exciton) or essentially localized at one atom or molecule (a Frenkel exciton). If excitons are produced by light absorption in a solar cell (step 1 in Chapter 1) and are to be utilized, then some process must also be present (step 2 in Chapter 1) to convert the exciton into at least one free negative charge carrier—one free positive charge carrier pair. (We return to this and specifically to the “at least one” part in Section 2.2.6.)

2.2.3.2 NANOPARTICLES AND NANOCRYSTALLINE SOLIDS

The single-electron energy levels can evolve in the case of nanoparticles and nanocrystals from the band picture of single-crystal, multicrystalline,

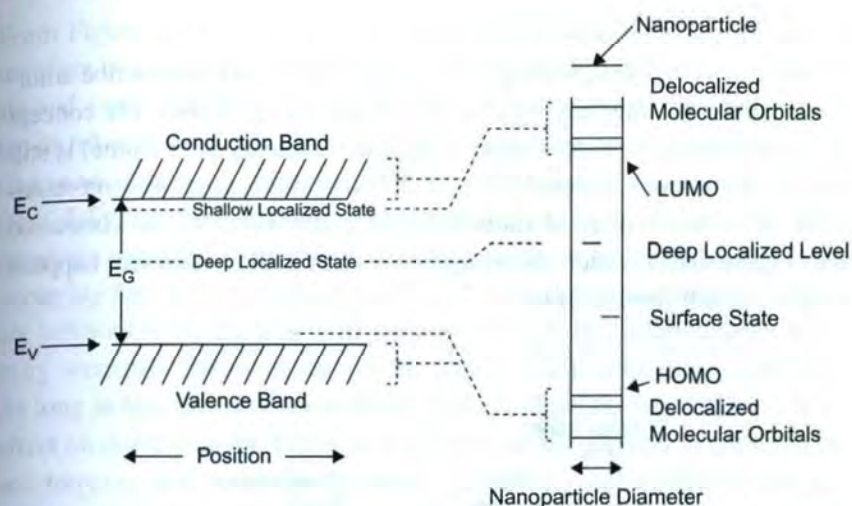


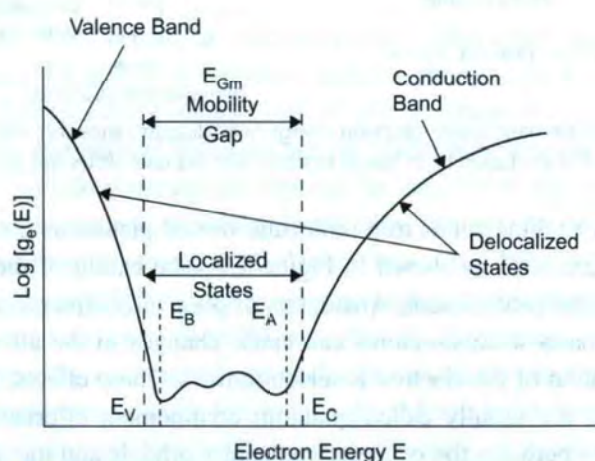
FIGURE 2.9 Schematic single-electron energy level diagram showing, with increasing confinement, the evolution from bands to molecular orbitals. (After Ref. 8.)

and microcrystalline solids to a molecular orbital picture as the size parameter is decreased,⁸ as shown in Figure 2.9. The extent of the evolution depends on the confinement. Analogous to phonon confinement, reducing the size of nano-scale structures can cause changes in the allowed states and a relaxation of the electron $\mathbf{k}$ -selection rules. These effects, in the case of electrons, are usually called quantum confinement effects. The spacing in energy between the occupied molecular orbitals and the unoccupied molecular orbitals (the energy gap) increases with confinement, as would be anticipated from the particle in a box problem. As may be noted from Figure 2.9, the highest occupied molecular orbital is called HOMO while the lowest unoccupied molecular orbital is called the LUMO. We will use this terminology from time to time in place of the corresponding terminology from solid-state physics and electrical engineering; i.e., valence band edge and conduction band edge. We also note that the energies and binding energies of excitons change in these materials with confinement.⁸

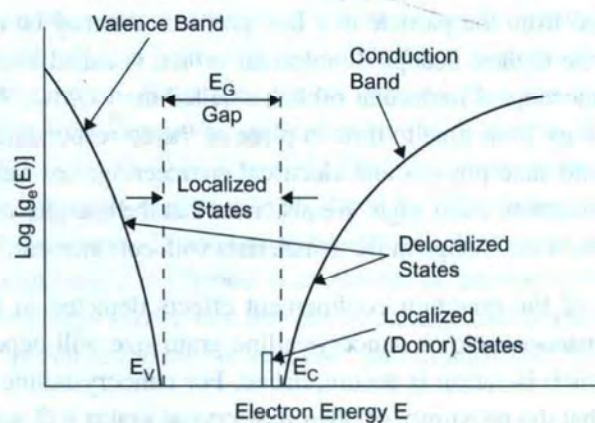
The impact of the quantum confinement effects depicted in Figure 2.9 for a given nanoparticle or nanocrystalline grain size will depend on the degree to which isolation is accomplished. For nanocrystalline materials, this means that the proximity of other nanocrystal grains will act to reduce the influence of quantum confinement. In the case of molecules, the quint-essential nanoparticles, interaction among the orbitals may allow transport from molecule to molecule.

2.2.3.3 AMORPHOUS SOLIDS

A band picture of the type seen in Figure 2.7 can be used to describe amorphous solids, but diagrams like Figure 2.6 are not applicable. The concept of density of electron states (states available per energy per volume) is still valid in amorphous materials. Figure 2.10a shows a schematic representation of such a density of states function $g_e(E)$. This may be contrasted with Figure 2.10b, which shows $g_e(E)$ for a crystalline solid that happens to have a donor level present.



(a)



(b)

FIGURE 2.10 Schematic showing the density of states function $g_e(E)$ for (a) an amorphous solid and (b) a crystalline solid.

From Figure 2.10 it is clear that amorphous materials can contain large numbers of localized gap states. These are essentially of two types: intrinsic and extrinsic. The intrinsic localized states are defined as arising from the distribution of bond angles and interatomic distances statistically occurring in an amorphous solid. Extrinsic localized states are defined as arising from defects (broken chemical bonds) and impurities. Intrinsic localized states are expected to be the principal contribution to the localized states occurring near the band edges (see Fig. 2.10a); defect and impurity states are believed to be the source of the large density of localized states typically seen over the remainder of the gap in many amorphous materials. As long as the density of these defect states is large, doping will have little effect on dislodging the Fermi level position in the gap and recombination and trapping will be severe problems. In the case of amorphous silicon, hydrogen is used to suppress the number of these states by forming chemical bonds to the defects. So much hydrogen is used that the material is actually a silicon-hydrogen alloy denoted as a-Si:H.

Since the localized state density is so large in many amorphous materials, transport via these gap states is possible; i.e., an electron can move from one localized site to another. We discuss this in detail later. It suffices to note at this point that transport via these localized states would give rise to small mobilities compared to transport involving the delocalized states. Hence, Figure 2.10a shows a mobility gap, which denotes the switch from small to larger mobilities, rather than a true gap. This mobility gap is expected to have sharp boundaries E_C and E_V , which serve as the demarcation between localized and delocalized states.

2.2.3.4 ORGANIC SOLIDS

Organic solids are usually classified as either small-molecule or polymeric solids. The molecular orbital picture (Fig. 2.9) is generally accepted as applicable for organic materials of either type. Both types of organics have been used in solar cells. In solids, the molecules interact to varying degrees, as noted earlier, and the result can be that, in some cases, the orbital levels form a band. While the density of delocalized states $g_e(E)$ of single-crystal and amorphous materials is parabolic as seen in Figure 2.10, at least near the band edges, the density of states $g_e(E)$ for organic materials is expected to have levels within a Gaussian-like envelope.⁹

2.2.4 Optical phenomena in solids

2.2.4.1 ABSORPTION PROCESSES

In this section we examine the photon interactions with solids that give rise to absorption. Figure 2.11 is a sketch showing the various processes that absorb electromagnetic radiation in solids and their range of influence. Process 1 in the figure is free-carrier absorption; it arises from photon-induced, electron (or hole) transitions within a band from one single-particle state to another. These intraband transitions, depicted diagrammatically in Figures 2.12a and b, are important in metals and semiconductors whenever there is a significant density of carriers in a band. Intraband transitions of the type seen in Figure 2.12a would be forbidden in crystalline solids (due to $\mathbf{k}$ conservation), were it not for the scattering processes (due to defects, impurities, phonons), which allow for the conservation of momentum. Process 2 of Figure 2.11 is phonon absorption; i.e., light is absorbed by exciting phonon modes in a material. Electrons are not involved in this process. Because of the low energies possessed by phonons (see Fig. 2.5), this absorption process occurs in the infrared region of a light spectrum.

Process 3 of Figure 2.11 includes all the photon-induced transitions between states in the gap as well as between gap states and a band. Example transitions are shown in Figures 2.12d and e. Process 4 is exciton-producing absorption. Absorption in organic materials, such as

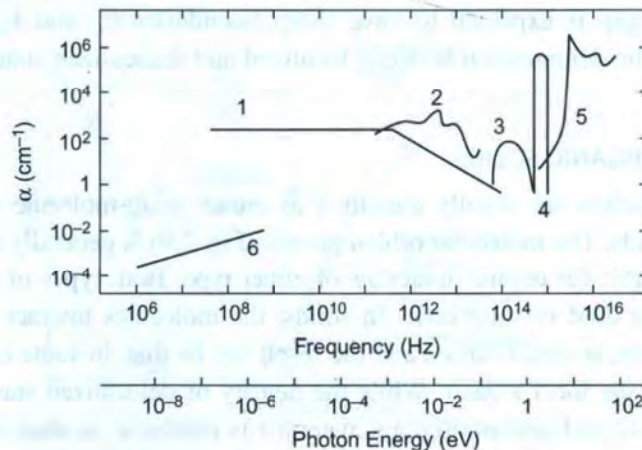


FIGURE 2.11 A schematic portrayal of the range of optical absorption processes in solids. The processes and the absorption coefficient α are discussed in the text.

the small-molecule dyes of dye-sensitized solar cells and the polymer absorbers of organic solar cells, is generally an exciton process. Excitons can also play the key role in absorption in nanoparticles. Process 5 is the band-to-band transitions, which are seen in Figure 2.12c. Process 6 is a loss observed in some amorphous materials; it probably arises due to electrons that are hopping (see Section 2.3.1.3) from localized site to localized site.¹⁰

The absorption coefficient $\alpha(\lambda)$ or equivalently $\alpha(\nu)$, which is the ordinate in Figure 2.11, is critical to solar cell performance. The Process 3, 4, and 5 contributions to α are the mechanisms we will be interested in because they can lead to free electrons and free holes. While Process 4 or Process 5 or both will be present in an absorber material, Process 3 may or may not be present at all. We can define a function $G(\lambda, x)$, which determines the number of Process 3, Process 4, or Process 5 events taking place at x per volume per time per bandwidth. This bandwidth is around the wavelength λ of the light impinging on the absorbing material.

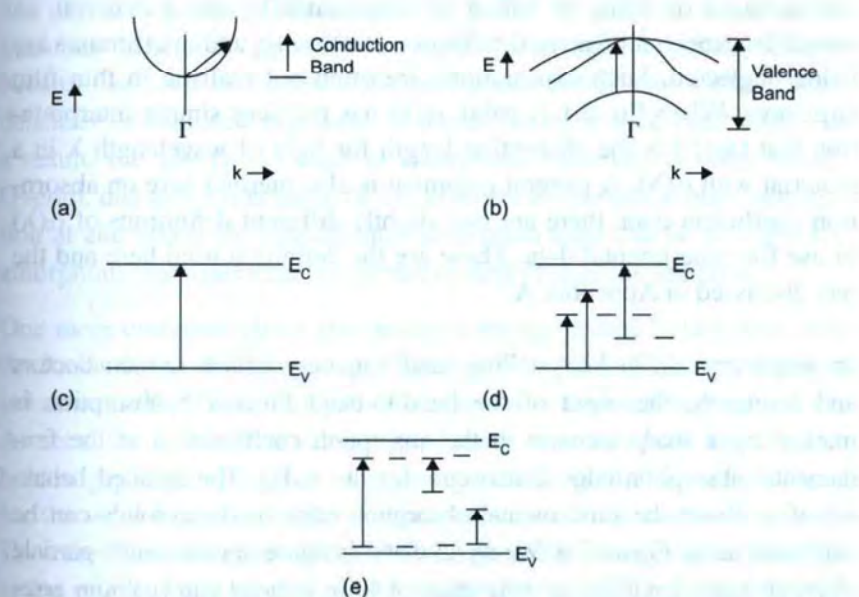


FIGURE 2.12 Electron transitions between single-electron states that give rise to light absorption: (a, b) free-carrier (intraband) transitions give rise to Process 1 of Figure 2.11; (c) band-to-band transitions give rise to Process 5; (d, e) band-localized-state transitions and localized-state-localized-state transitions are the source of Process 3. The type of Process 3 seen in (d) can give rise to free carriers.

It can be shown that $G(\lambda, x) \propto \alpha(\lambda, x)\xi^2(\lambda, x)$, where $\xi(\lambda, x)$ is the (optical frequency) electric field of light of wavelength λ at point x .¹¹

If reflection and interference wave effects are not important in a solar cell structure, then monochromatic light entering into the cell's absorber at $x = 0$ with intensity $I_0(\lambda)$ (photons per area per time per bandwidth) is expected to have the intensity $I(\lambda, x)$ at some point x in the material given by¹⁰

$$I(\lambda, x) = I_0(\lambda)e^{-\alpha(\lambda)x} \quad (2.1)$$

Equation 2.1 is known as the Beer-Lambert law. This expression, when valid, allows $G(\lambda, x)$ to be written as

$$G(\lambda, x) = \alpha(\lambda)I_0(\lambda)e^{-\alpha(\lambda)x} \quad (2.2)$$

since the spatial derivative of Eq. 2.1 gives the photons lost. Comparison with the more general expression above shows that the Beer-Lambert law is based on $\xi^2(\lambda, x)$ falling off exponentially into a material, as would be expected if internal reflection, scattering, and interference are being neglected. Such expectations are often not realistic in thin film structures. When Eq. 2.1 is valid, $\alpha(\lambda)$ has the very simple interpretation that $1/\alpha(\lambda)$ is the absorption length for light of wavelength λ in a material with $\alpha(\lambda)$. A general comment is also merited here on absorption coefficient data: there are two slightly different definitions of $\alpha(\lambda)$ in use for experimental data. These are the definition used here and the one discussed in Appendix A.

In single-crystal, multicrystalline, and microcrystalline semiconductors and insulators, the onset of the band-to-band Process 5 absorption is marked by a sharp increase in the absorption coefficient α at the fundamental absorption edge that occurs for $h\nu = E_G$. The detailed behavior of α above the fundamental absorption edge in these solids can be explained using Figure 2.6. We recall that this figure depicts single-particle electron states available, as a function of $\mathbf{k}$, in a direct-gap (gallium arsenide) and in an indirect-gap (silicon) crystalline semiconductor. In direct-gap material, an electron can be excited from the top of the valence band to the bottom of the conduction band with essentially no change in $\mathbf{k}$ -vector required. Since a photon has a $\mathbf{k} \approx 0$ on the scale of Figure 2.6

to contribute to the momentum, there is no difficulty in $\mathbf{k}$ -vector conservation in electron-photon interactions that result in an electron's being excited across a direct gap. This is not the case for an indirect-gap material, as Figure 2.6 also shows. In this case, an electron excited across an indirect gap must change its $\mathbf{k}$ -vector. The photon simply cannot supply the momentum; hence phonon involvement is required. As seen in Figure 2.5, phonons can supply the necessary momentum but conservation of total energy and total momentum for the three particles (electron, photon, and phonon) must now apply. The necessity of a three-body interaction in indirect-gap materials tends to lessen the magnitude and crispness of $\alpha = \alpha(\lambda)$ at and above the fundamental absorption edge. This issue of conserving the total $\mathbf{k}$ -vector during band-to-band transitions can disappear for small-enough crystalline nanoparticles and nanocrystalline materials for two reasons: the constraint of a well-defined $\mathbf{k}$ -vector can disappear for phonons and electrons with confinement, as we have discussed. Because of this, nanocrystalline silicon, for example, exhibits stronger absorption than its single-crystal, multicrystalline, and microcrystalline counterparts.⁶

The distinction among Processes 3, 4, and 5 of Figure 2.11 generally becomes difficult to discern from $\alpha(\lambda)$ for amorphous solids. This is because, as seen in Figure 2.10, amorphous solids can contain large densities of localized gap states at the delocalized state band edge. As a result, the absorption edge in amorphous materials is often broad. Overall, due to the relaxation of the $\mathbf{k}$ -vector conservation rules, absorption at and above the fundamental absorption edge can be stronger for amorphous materials than for corresponding crystalline material.

One more comment about absorption: a strong electric field ξ , can shift the fundamental absorption edge (Process 5) in solids. This phenomenon is known as the Franz-Keldysh effect, and it is depicted in Figure 2.13. As seen, the delocalized valence-band wave functions leak into the forbidden gap in the presence of a strong electric field. The same is true for the wave functions of the delocalized states in the conduction band. Therefore there is a probability P that a photon can promote an electron at the valence band edge at point x to the conduction band edge at point x' . The electric field dependence of this probability goes as¹²

$$P \sim \exp - \left(\frac{E'}{E_0} \right) \quad (2.3)$$

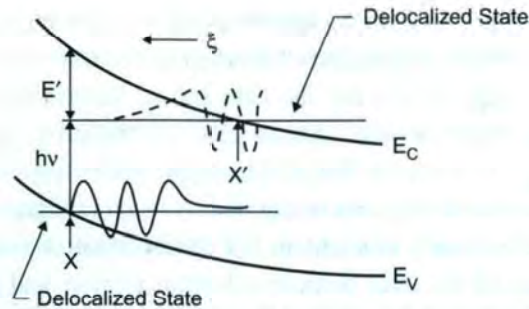


FIGURE 2.13 Franz-Keldysh effect allows band-to-band absorption for $h\nu < E_G$. As shown, the process involves tunneling and photon absorption in the presence of an electric field ξ .

where in this case E_0 stands for

$$E_0 = \frac{3}{2} (m^*)^{-1/3} (e\hbar\xi)^{2/3} \quad (2.4)$$

Here the energy E' is defined at x in Figure 2.13, m^* is the effective mass, and ξ is the electric field. As seen in Figure 2.13, an electron in the valence band can make the transition into such a tail from the conduction band with the absorption of a photon $h\nu < E_G$. This gives rise to the shift in the fundamental absorption edge. In amorphous materials one would expect such tails could extend further into the gap due to overlapping with localized gap states. In addition, Figure 2.13 does not consider any possible exciton role.

2.2.4.2 INTERFERENCE, REFLECTION, AND SCATTERING PROCESSES

While we have been discussing photons, the “particles” of light, and their interaction with materials, the wave properties of light are also very important in solar cell structures. Illumination of wavelength λ can be reflected as it enters a cell and it can undergo additional reflection at each interface. Interference patterns can be set up within the cell. Scattering can occur at small structures or features. An example of contrasting $G(\lambda, x)$ behavior that can result from the varying importance of these wave phenomena is presented in Figure 2.14 for two values of λ . These two values of λ are impinging on an organic heterojunction solar cell.¹¹ As is shown, exponentially varying $G(\lambda, x)$ behavior with position in the absorber, as predicted from the Beer-Lambert law, is followed reasonably well for $\lambda = 300$ nm. This is due

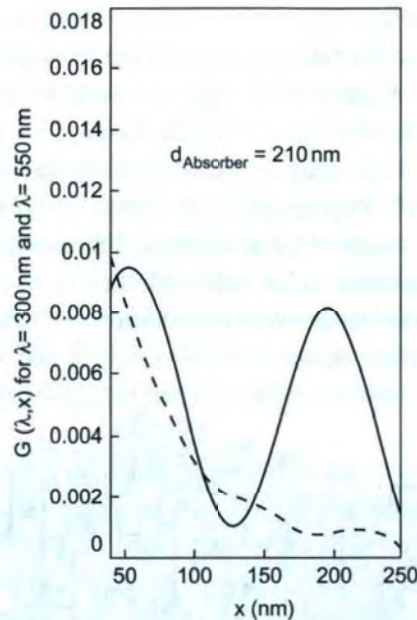
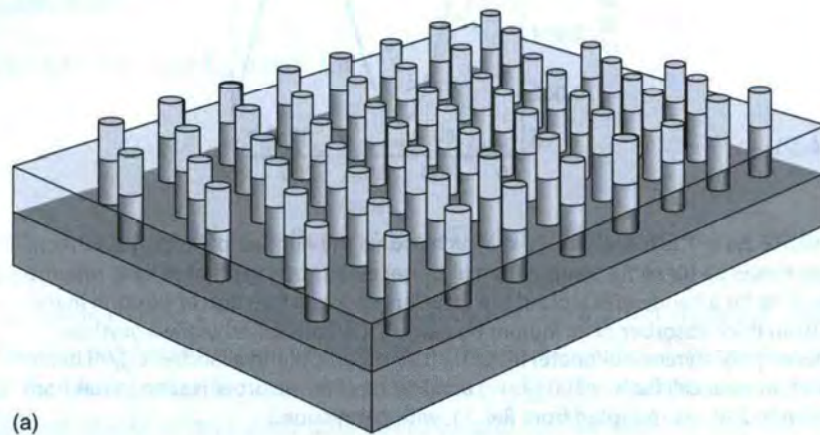


FIGURE 2.14 The function $G(\lambda, x)$, which counts the number of Process 3, Process 4, or Process 5 (or some combination of these) events taking place at x per volume per time for a bandwidth around the wavelength λ as a function of position in the 210 nm thick absorber of an indium tin oxide (ITO)/Poly(3,4-ethylenedioxythiophene)-poly(styrene-sulfonate) (PEDOT-PSS)/ organic blend absorber/ C_{60} /Al heterojunction solar cell for $\lambda = 300$ (—) and 550 nm. The absorber is seen to run from 40 nm to 250 nm. (Adapted from Ref. 11, with permission.)

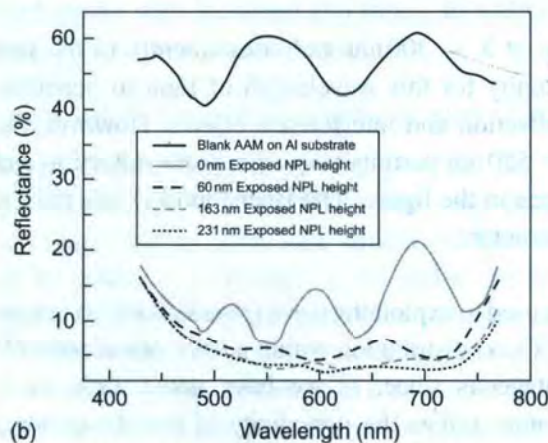
to very strong absorption at $\lambda = 300$ nm and consequently to the fact that there is little opportunity for this wavelength of light to penetrate to interfaces to set up reflection and interference effects. However, the weaker absorption at $\lambda = 550$ nm permits very significant reflection and interference effects, as seen in the figure. The Beer-Lambert law fails at this wavelength for this structure.

Photonic structures can be used to exploit the wave (physical optics) behavior of light to shape the $\xi^2(\lambda, x)$ distribution within a solar cell absorber.¹³ This can be very advantageous since, as we have noted, $G(\lambda, x) \propto \alpha(\lambda)\xi^2(\lambda, x)$. These structures utilize the periodicity of two-dimensional or three-dimensional “photonic crystals”, composed of repeating regions of materials with differing dielectric constants, to control light.¹⁴ The length-scale of the periodicity of these photonic crystal structures must be a significant fraction of the wavelength of the light to be manipulated.¹⁵

Given the wavelengths of the photon-rich part of the solar spectrum (Fig. 1.1), these structures must have features at the nano-scale (i.e., $\sim 100\text{ nm}$) or somewhat larger. Figures 2.15a and b show an example of using such a photonic crystal structure to affect reflectance. This particular example shows the impact of an array of CdS nanocolumns of different heights on reflectance of light impinging on the array. These experimental light-trapping data were obtained prior to the addition of CdTe to fabricate a CdS-CdTe heterojunction solar cell with the CdS nanocolumns. The reflectance changes somewhat with the addition of CdTe.¹⁶



(a)



(b)

FIGURE 2.15 (a) An array of CdS nano-pillars (NPLs) grown in an anodized aluminum (AAM) template. Center-to-center spacing is about 150 nm. (b) Experimentally measured reflectance from such an array, with the NPLs protruding from the AAM template at heights of 0, 60, 163, and 231 nm. (From Ref. 16, with permission.)

Texturing at contacts of a cell with features on the order of a micron can also lead to light trapping and reduced reflection from the cell. This light trapping is easily explained using geometrical optics (beam tracing) and the recognition that there will be longer path lengths through the absorber for light entering front texturing or reflected at the back texturing. The longer path lengths lead to more absorption. The approach becomes problematic for thin-film solar cells, since the absorber thickness can be of the order of, or smaller than, the texturing features required.^{15,17} The photonic crystal approach is totally different, since it relies on physical optics phenomena (reflection, interference, and diffraction) and employs much smaller structures.¹⁵

Plasmonics is another phenomenon that offers interesting potential for solar cell applications.¹⁷ The term refers to the cooperative electron oscillations (quantized into plasmons) that can be set off by light impinging on nano-scale metal features (e.g., nanoparticles, etched structures) and the re-radiation of light (scattering) from these features.^{1,17} In the case of solar cell structures, it also appears that there can be a coupling of this re-radiated light into the waveguide modes that can exist in a cell structure and the feedback of the light into the metal features.¹⁷ Plasmonic effects can give rise to very strong near fields in the immediate vicinity of the metal features, resulting in greatly enhanced absorption in these volumes.¹⁸ Consequently, plasmon scattering can be designed to create an advantageous $\xi^2(\lambda, x)$ distribution and thereby to enhance absorption and control its distribution. A listing of calculated plasmon frequencies, expressed as wavelengths, for selected metal nanoparticles (in a medium of index of refraction of 1.33) is found in Table 2.2.¹⁹ Light at or near the wavelengths listed in Table 2.2 can couple into the plasmon scattering mechanism. These wavelengths listed in the table can shift due to medium, substrate, and waveguide effects.¹⁷ Both randomly arranged metal nanoparticles and periodic metal nano-scale features ("plasmon crystals") have been used to modify the $\xi^2(\lambda)$ distribution in solar cells by exploiting the plasmon effect. In the case of metal nanoparticles, several nanoparticle positioning schemes have been explored, including placing the metal nanoparticles at and near the material interface in heterojunctions²⁰ and placing the particles in a two-dimensional lattice on the top (light-entering) surface of a cell.²¹ Figures 2.16a and b show the results of a simulation study for an a-Si:H p-i-n cell with Au nanoparticles positioned on the top surface, as shown in

Table 2.2 Some Plasmon Wavelengths

Metal	Localized surface plasmon (resonance) wavelength (nm)
Pd	~250
Ag	~390
Ba	~400
Eu	~380 (with a shoulder to ~500)
Ca	~500
Y	~430 (broad peak)
Au	~525
Pt	~230
Cu	~210 (with a shoulder to ~580)
Cs	>700

From Ref 19.

Figure 2.16a. In such an a-Si:H cell, the red and near infrared wavelength photons ($\lambda > 650\text{nm}$) have very long absorption lengths (exceeding $1\mu\text{m}$) and normally cannot be efficiently absorbed by the 500-nm a-Si:H absorber used in the simulation. However, absorption is enhanced in Figure 2.16b across a range of light wavelengths (except for those near or at $\lambda = 500\text{nm}$) when 70–80nm radius Au nanoparticles with a separation (pitch) of 650nm are present. The disadvantageous behavior at $\lambda \sim 500\text{nm}$ is due to reflection at the top surface for these wavelengths.²¹ Similar simulations have found that the use of a two-dimensional metal “plasmon crystal” with nano-scale features at the back of a cell (see Fig. 2.17) can avoid loss of long-wavelength absorption and actually enhance absorption in this range, as seen in Figure 2.17.²¹ The deleterious short-wavelength (values around 500nm) loss seen for the nanoparticle case in Figure 2.16 does not appear here since these short wavelength photons are absorbed before they reach the back of the cell.

2.2.5 Carrier recombination and trapping

Carriers, free electrons in a semiconductor conduction band (CB) and the free holes in a semiconductor valence band (VB), are what are

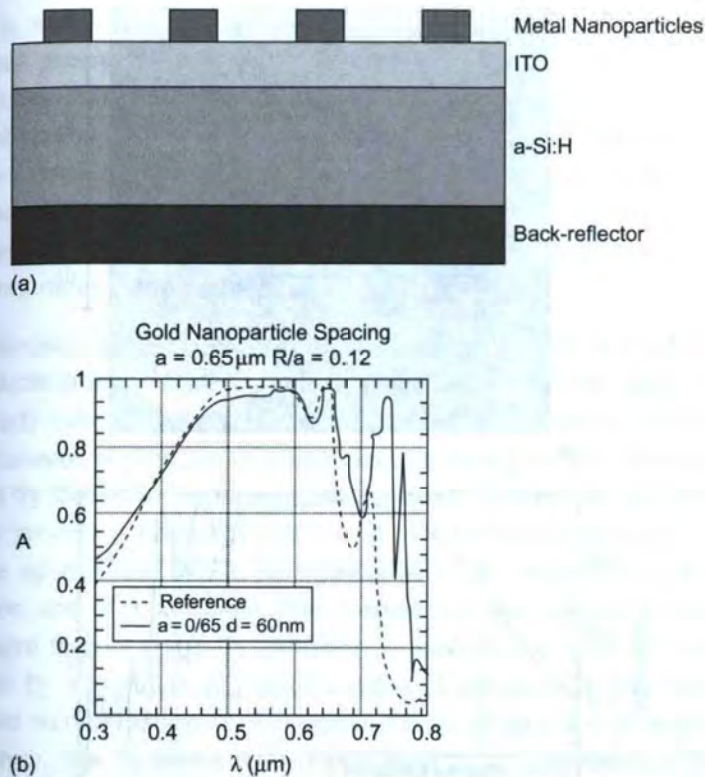


FIGURE 2.16 (a) Diagram of a nanoparticle-coated a-Si:H solar cell. (b) Absorption simulation results for this cell with nanoparticles present (solid line) and for the corresponding cell with no nanoparticles present (dashed line). The a-Si:H absorber layer thickness was taken to be 0.5 μm . The low absorption at short wavelengths is due to front surface reflection. (From Ref. 21, with permission.)

needed to make a solar cell work. Once electrons are excited to the conduction levels and the corresponding holes are created in the valence levels, or once excitons dissociate, producing electrons in the conduction levels and holes in the valence levels, the aim is to get them to do work via Step 3 of Chapter 1. However, excited electrons can return to their ground state or drop in energy into some gap state without doing anything useful. This can happen in one of several ways: an electron can give up its energy through a radiative mechanism (radiative recombination), which involves emission of a photon (this may or may not also involve phonons); an electron can give up energy by emission of phonons, a process which involves gap states too (Shockley-Read-Hall or gap-state-assisted recombination); or an electron can give up its energy through an Auger mechanism (Auger recombination), which involves

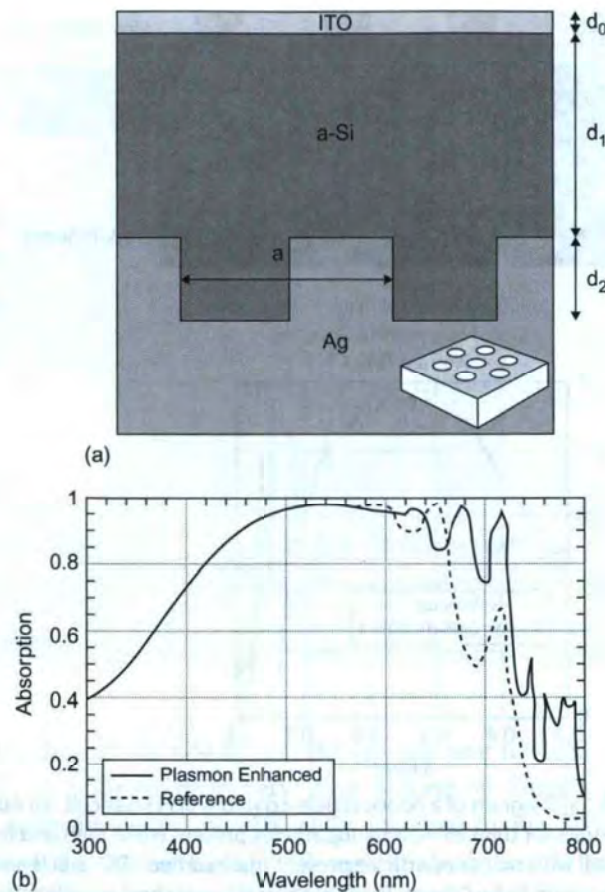


FIGURE 2.17 (a) A Ag “plasmon crystal” at the back of an a-Si:H solar cell. (b) Absorption simulation results for this cell with plasmon crystal present (solid line) and for the corresponding cell with no plasmon crystal present (dashed line). The a-Si:H absorption layer thickness is taken to be $d_1 = 0.5 \mu\text{m}$. The plasmon crystal has a lattice pitch $a \sim 750 \text{ nm}$ and an etch depth d_2 of 200 nm. The radius of the holes is taken to be 225 nm. The low absorption seen at short wavelengths is due to front surface reflection. (From Ref. 21, with permission.)

the transfer of its energy to another electron or hole. Multi-particle states also have similar mechanisms. For example, excitons can lose energy by radiation or by an Auger process (Auger recombination). These three general recombination mechanisms all have corresponding opposite processes; these are thermal generation mechanisms. Recombination and thermal generation are always present in a material or device. Photogeneration can also be present under illumination. In thermodynamic equilibrium (TE),

there is no applied or developed voltage, illumination, nor temperature gradient present. The principle of detailed balance applies in TE and it requires that each thermal generation process and its corresponding recombination process statistically balance one another. When additional (excess) carriers are created in a material, as occurs under light or carrier injection (due to biasing), the material is no longer in the state of TE and there is net recombination, where net recombination is defined as recombination minus thermal generation.

Free electron-hole recombination has the overall result of annihilating a free electron in the conduction band and a free hole in the valence band. In steady-state operation, which is what we are interested in, it is the simultaneous wiping out of a free electron-hole pair. Recombination is driven by the carrier populations in the bands. A unimolecular recombination process is driven by just n or p . A bimolecular process is driven by the np product. While recombination is the annihilation of a free electron and of a free hole, free carriers are also subject to trapping. The term trapping, strictly speaking, is used in two ways: (1) to mean capture by a gap state as part of a series of processes in localized state assisted recombination or (2) to mean the act of an electron or hole getting stuck at a localized state. When used in the latter sense, trapping is the stringing together of one or more energy-loss processes with the net result that an electron from the conduction band or a hole from the valence band finds itself in a deadend in a gap state. Recombination, when it is localized state assisted, can involve gap states existing in the bulk, at surfaces, and at grain boundaries of materials. Trapping involves these gap states too. Carriers in gap states, whether there due to trapping or passing through in a recombination process, give rise to charge according to the state occupation and to whether the states are acceptor-like, donor-like, or amphoteric.

2.2.5.1 RECOMBINATION MODELING

(a) Radiative recombination

As discussed in detail in Appendix B, net radiative recombination for free electrons and holes may be expressed as

$$\mathcal{R}^R = \left(\frac{g_{th}^R}{n_i^2} \right) (pn - n_i^2) \quad (2.5)$$

where n_i^2 , the square of intrinsic number density, is always equal to $n_0 p_0$ (the subscript zero refers to thermodynamic equilibrium (TE) values), whether a material is intrinsic or extrinsic.³ The dimensions of $\mathcal{R}^R$ are number (of free holes or equivalently of free electrons) annihilated per volume per time. Obviously, $\mathcal{R}^R$ is zero in TE.

If a material is p-type and if, even under illumination, p is still essentially p_0 , then Eq. 2.5 can be written as

$$\mathcal{R}^R = \left(\frac{g_{th}^R}{n_i^2} \right) (np_0 - n_0 p_0) \quad (2.6)$$

Defining $[p_0 g_{th}^R / n_i^2]^{-1}$ as τ_n^R allows Eq. 2.6 to be finally written as

$$\mathcal{R}^R = \frac{n - n_0}{\tau_n^R} \quad (2.7)$$

where τ_n^R is called the electron radiative recombination lifetime or simply the electron lifetime, if this mechanism dominates over other recombination paths. Similarly, if a material is n-type and if, even under illumination, n is still essentially n_0 , then it follows that Eq. 2.5 can be written as

$$\mathcal{R}^R = \frac{p - p_0}{\tau_p^R} \quad (2.8)$$

where $\tau_p^R = [n_0 g_{th}^R / n_i^2]^{-1}$ and is called the hole radiative recombination lifetime or simply the hole lifetime, if this is the dominant recombination mechanism. When these linearized forms of Eq. 2.5 (Eqs. 2.7 and 2.8) can be utilized, the bimolecular process of radiative recombination becomes controlled by one carrier; i.e., it becomes unimolecular.

(b) Shockley-Read-Hall recombination

As we noted, a second process by which free electrons and holes can relax to lower energies and recombine involves phonon emission. As may be seen from Figure 2.5, phonons have energies ≤ 0.1 eV and consequently band-to-band recombination strictly by simple phonon emission would require essentially simultaneous multiple-phonon involvement, which is

believed to be unlikely. However, the situation changes if we bring in the localized states present in the material. Charge carriers can give up their energy in collisions with the physical entity that gives rise to this localized level, and become trapped by it. The energy may be released in this collision (trapping) event as phonons or photons or both. The trapping of an electron, for example, and then the trapping of a hole completes the recombination. This what we have called gap-state or equivalently localized-state assisted recombination. We use the symbol $\mathcal{R}^L$ for the net recombination rate from such processes. The superscript emphasizes the role played by localized gap states. This mechanism is termed Shockley-Read-Hall (S-R-H) recombination.³

As shown in Appendix C, the quantity $\mathcal{R}^L$, the net recombination through gap states at energy E , can be expressed in steady state as

$$\mathcal{R}^L = \frac{v\sigma_n\sigma_p N_T (np - n_i^2)}{\sigma_p(p + p_1) + \sigma_n(n + n_1)} \quad (2.9)$$

where σ_n is the capture cross-section (attractiveness) of these states for electrons and σ_p is their capture cross-section (attractiveness) for holes. If a material is p-type and if, even under illumination, p is still essentially p_0 , then Eq. 2.9 can be written as

$$\mathcal{R}^L = \frac{v\sigma_n\sigma_p N_T (np_0 - n_0p_0)}{\sigma_p(p_0 + p_1) + \sigma_n(n + n_1)} \quad (2.10)$$

or as

$$\mathcal{R}^L = \frac{v\sigma_n\sigma_p N_T p_0 (n - n_0)}{\sigma_p(p_0 + p_1) + \sigma_n(n + n_1)} \quad (2.11)$$

Defining $\tau_n^L = [v\sigma_n\sigma_p N_T p_0 / \sigma_p(p_0 + p_1) + \sigma_n(n + n_1)]^{-1}$ and assuming it does not depend strongly on n finally allows Eq. 2.9 to be linearized to

$$\mathcal{R}^L = \frac{n - n_0}{\tau_n^L} \quad (2.12)$$

where τ_n^L is called the electron S-R-H recombination lifetime or simply the electron lifetime, if this is the dominant recombination mechanism. Similarly, if a material is p-type and if, even under illumination, n is still essentially n_0 , then it follows that Eq. 2.9 can be linearized to

$$\mathcal{R}^L = \frac{p - p_0}{\tau_p^L} \quad (2.13)$$

where $\tau_p^L = [v\sigma_n\sigma_p N_T n_0 / \sigma_p(p + p_1) + \sigma_n(n_0 + n_1)]^{-1}$, assumed not to depend strongly on p , is the hole S-R-H recombination lifetime or simply the hole lifetime, if this is the dominant recombination mechanism. The linearization that takes Eq. 2.9 to 2.12 or 2.13, when valid, causes the mechanism to move from being bimolecular to being unimolecular; i.e., to being driven by one carrier.

It must be stressed that all of the above equations for S-R-H recombination have been written for one localized state group at some energy E in the energy gap. If a gap state distribution is present, there must be corresponding statements for the other gap states at other energies. Therefore, the total S-R-H recombination must be the sum of all these contributions. This requires that the above equations all become sums over the distribution.

(c) Auger recombination

The distinguishing feature of an Auger mechanism is that electrons and holes or excitons take energy from, or give energy to, other electrons and holes or excitons. There are many types of Auger processes. Some of the single-particle paths, from among many possible, are seen in Figure 2.18.²² Process (a) of the figure shows an electron-hole Auger recombination process in which an electron falls from the conduction band to the valence band by giving its energy to another electron in the conduction band. We expect the Auger recombination rate r_A^A for this path to obey $r_A^A = A_{1A}^A n^2 p$. The corresponding generation process has an energetic electron in the conduction band relaxing to the band edge and generating an electron-hole pair with the released energy. It may be modeled as $g_A^A = A_{2A}^A n$. This corresponding Auger generation process is often called impact ionization.³ Process (b) of the figure shows the equivalent Auger recombination process for a case in which a hole takes away the energy. It follows that we

would expect $r_B^A = A_{1B}^A n p^2$ for this path. The corresponding generation process has an energetic hole in the valence band relaxing to the band edge and generating an electron-hole pair with the released energy. It may be modeled as $g_B^A = A_{2B}^A p$. This too can be termed impact ionization. Processes (c)–(f) are not, of themselves, recombination processes, since an electron-hole pair does not disappear. As can be seen, (c)–(e) get carriers into or out of localized states; i.e., they cause trapping or de-trapping. Process (f) allows a trapped carrier to drop down lower in energy. Parts (c), (d), and (f) of the figure show localized state analogues to process (a) with $r_C^A = A_{1C}^A n^2 \tilde{p}_T$, $r_D^A = A_{1D}^A \tilde{n}_T n p$ and $r_F^A = A_{1F}^A n \tilde{n}_T \tilde{p}_T$. Obviously there are free hole equivalents to these paths. Process (e), which results in the de-trapping of two carriers, can be modeled by $r_E^A = A_{1E}^A \tilde{n}_T^2 p$. As explained also in Appendix C, $\tilde{p}_T$ counts the single electron states per volume at energy E that are missing an electron and $\tilde{n}_T$ counts the single electron states per volume at energy E that are occupied by an electron. The quantity $\tilde{p}_T$ contributes to the p_T in the expression $e p_T$ for gap-state positive space charge density only if the empty states are donor-like. The quantity $\tilde{n}_T$ contributes to the n_T in the expression $-e n_T$ for gap-state negative space charge density only if the occupied states are acceptor-like.

As we see from our discussion of Figure 2.18, there are two free-carrier Auger recombination processes. We can develop models for them by first using the principle of detailed balance to relate A_{1A}^A with A_{2A}^A for process (a) and to relate A_{1B}^A with A_{2B}^A for process (b). These relationships, with some straightforward algebra, then allow the net recombination for process (a), $\mathcal{R}^{AA}$, and the net recombination for process (b), $\mathcal{R}^{AB}$, to be written as

$$\mathcal{R}^{AA} = A_{2A}^A \left[\frac{n^2 p}{n_0 p_0} - n \right] \quad (2.14a)$$

and

$$\mathcal{R}^{AB} = A_{2A}^A \left[\frac{p^2 n}{n_0 p_0} - p \right] \quad (2.14b)$$

The strong dependence seen in Eq. 2.14 on n or p means Auger recombination can become dominant in solar cells at high carrier concentrations.

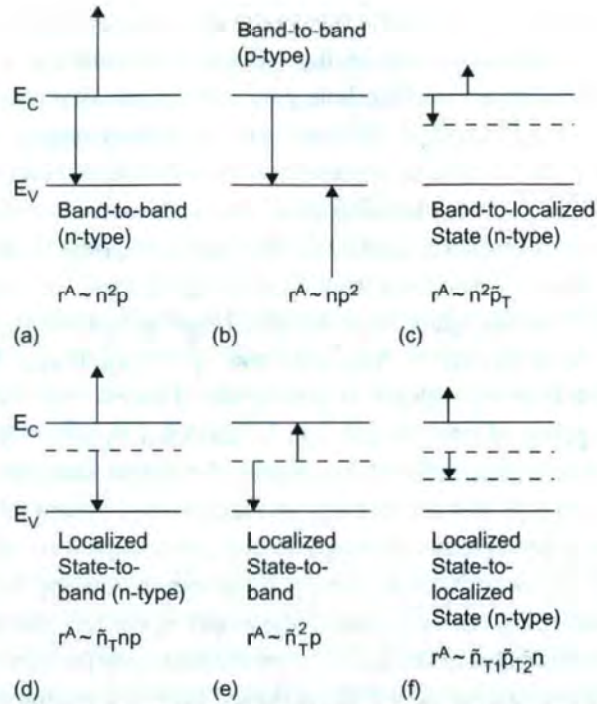


FIGURE 2.18 Some possible Auger transition processes in solids. The dependence of the different energy loss paths on the various number densities involved is indicated. Here $\bar{p}_T$ gives the number of empty localized states at energy E per volume and $\bar{n}_T$ gives the number of occupied localized states at energy E per volume. (Adapted from Ref. 22.)

Often it is hoped that the above expressions for Auger recombination can be adequately represented by a linearized model and that the processes of Eq. 2.14 can be written as

$$\mathcal{R}^A = \frac{n - n_0}{\tau_n^A} \quad (2.15a)$$

for p-type material and as

$$\mathcal{R}^A = \frac{p - p_0}{\tau_p^A} \quad (2.15b)$$

for n-type material. When this is done, τ_n^A and τ_p^A are the electron and hole Auger lifetimes.

Table 2.3 Differences between $G(\lambda, x)$ and $G_{ph}(\lambda, x)$

Phenomenon	Comments
Intermediate band absorption	Can allow Process 3 of Figure 2.11 to contribute to $G_{ph}(\lambda, x)$
Exciton dissociation	Must occur for exciton contribution to $G(\lambda, x)$ to appear in $G_{ph}(\lambda, x)$
Auger multiplication	For example, energetic excitons can undergo Auger process, producing a second exciton, and thereby the possibility of carrier multiplication.

2.2.6 Photocarrier generation

The function $G(\lambda, x)$ was introduced in Section 2.2.4.1 to count the number of Process 3, Process 4, and Process 5 absorption events at some point x in an absorber due to light of wavelength λ . $G(\lambda, x)$ is not necessarily the photocarrier generation function $G_{ph}(\lambda, x)$ per volume per time because of the three reasons listed in Table 2.3. First, some part of the Process 3 contribution to $G(\lambda, x)$ may be found in $G_{ph}(\lambda, x)$ but only if there are gap states of sufficient number and of sufficiently advantageous energy position to assist in carrier promotion from the VB to the CB by photons. Gap states need to be present in large numbers to ensure a significant contribution from this path and, if so, may form an intermediate band (IB). If there are enough gap states present, however, there may be a down side: the possibility of enhanced recombination. With a properly energetically positioned IB, VB-IB and subsequent IB-CB transitions can possibly lead to a net positive effect of enhanced carrier generation, due to the involvement of sub-band gap photons.²³ Turning to Processes 4 and 5, we note that the Process 5 contribution to $G(\lambda, x)$ shows up directly in $G_{ph}(\lambda, x)$. In the case of Process 4, the excitons produced must dissociate into free carriers to contribute to $G_{ph}(\lambda, x)$. This can be accomplished at heterojunction interfaces and, in principle, at regions of high electric fields. However, the latter possibility is reported by some to be inconsequential.²⁴ Where and to what degree exciton dissociation happens determine the Process 4 component of $G_{ph}(\lambda, x)$. For example, when exciton dissociation occurs at an interface, electrons appear on one side of the interface and holes on the other. In that case $G_{ph}(\lambda, x)$ becomes two expressions: $G_{ph}^n(\lambda, x)$ and $G_{ph}^p(\lambda, x)$. This will be addressed further in subsequent chapters.

The Process 4 contribution can, in principle, also be amplified by Auger exciton multiplication in a manner analogous to the single-carrier Auger generation mechanism corresponding to process (a) of Figure 2.18. That is, an energetic exciton can relax in energy to a lower state by creating a second exciton.²⁵ This process can occur in semiconductor nanoparticles (quantum dots) and is usually termed carrier multiplication.²⁵ Strictly speaking, the carrier population has not been multiplied until the excitons dissociate.

2.3 TRANSPORT

2.3.1 Transport processes in bulk solids

Thinking of semiconductors as being composed of a bulk and interface (e.g., contact and grain boundary) portion allows us to address transport systematically in these regions. We undertake the modeling of bulk-region conduction band and valence band transport in this book using the concepts of drift and diffusion. The assumptions behind, and the development of, this drift-diffusion formalism are presented in detail in Appendix D. The key transport equations that come out of the drift-diffusion approach of Appendix D are summarized here for convenience. These equations are rigorously valid for single-crystal solids. In cases of multicrystalline and microcrystalline inorganic solids, the drift-diffusion model is strictly valid within crystals so long as the scattering length is less than the characteristic dimension of the crystal. In polycrystalline materials, intragrain drift-diffusion transport may be in series with injection, recombination, or tunneling processes at grain boundaries. For nanocrystalline materials, a drift-diffusion model can suffice by using an effective mobility, which depends on grain size. The drift-diffusion approach also works well for amorphous inorganic and amorphous and crystalline organic materials. In the case of amorphous materials, there can also be transport via the gap states in parallel with conduction band and valence band transport. For organic materials, transport between molecules controlled by tunneling mechanisms can dominate in some cases. For nanoparticles, transport is expected to be interface dominated and also to depend on the matrix in which the particles are imbedded. In the latter two situations, carriers may have to percolate through a solid as they search for optimum interface tunneling paths.

2.3.1.1 BULK REGION CONDUCTION BAND TRANSPORT

As established in Appendix D, the general expression for $n(x)$, the free electron population per volume in the conduction band at some point in a material system, which is valid even when out of TE, is given by

$$n = \int_{E_c}^{\infty} \left[\frac{1 + \exp(E - E_{Fn})}{kT_n} \right]^{-1} A_c(E - E_c)^{1/2} dE \quad (2.16)$$

In this expression, E_{Fn} is the spatially varying electron quasi-Fermi level, T_n is the spatially varying electron temperature, and $A_c(E - E_c)^{1/2}$ is a model for the conduction band density of states $g_c(E)$. The quantity A_c may vary with position. This parabolic model for the conduction band density of states is rigorously valid for crystalline and polycrystalline materials and works well for amorphous inorganics, too. A Gaussian distribution is probably more appropriate for organics. Equation 2.16 may be simplified to

$$n = N_C \exp \left[\frac{-(E_c - E_{Fn})}{kT_n} \right] = N_C \exp \left[\frac{-V_n}{kT_n} \right] \quad (2.17)$$

if the electron quasi-Fermi level E_{Fn} lies at least several kT_n below E_c . In Eq. 2.17, N_C is the conduction band effective density of states and the quantity V_n locates the conduction band edge with respect to the electron quasi-Fermi level at point x (see Appendix D). When the criterion for the use of Eq. 2.17 is fulfilled, Boltzmann statistics, rather than Fermi-Dirac, is being used to determine the conduction band population.

It follows from Appendix D that the conventional current density J_n being carried by these n electrons per volume at point x can be written as

$$J_n = e\mu_n n \frac{dE_{Fn}}{dx} - en\mu_n S_n \frac{dT_n}{dx} \quad (2.18)$$

where the material parameters μ_n and S_n are the electron mobility and Seebeck coefficient, respectively. In Eq. 2.18 both drift and diffusion are built into the quasi-Fermi level gradient term. As also shown in Appendix D, Eq. 2.18 can be rewritten as

$$J_n = e\mu_n n \left(\xi - \frac{d\chi}{dx} - kT_n \frac{d \ln N_C}{dx} \right) + eD_n \frac{dn}{dx} + eD_n^T \frac{dT_n}{dx} \quad (2.19a)$$

or alternatively as

$$J_n = e\mu_n n\xi + e\mu_n n\xi'_n + eD_n \frac{dn}{dx} + eD_n^T \frac{dT_n}{dx} \quad (2.19b)$$

Equations 2.19a and b explicitly use the parabolic density of states model but have equivalent forms for other density of states models. Equation 2.19b clearly shows the drift and diffusion components. The electron diffusion coefficient D_n and the electron thermal diffusion coefficient (or Soret coefficient) D_n^T have been introduced into Eqs. 2.19a and b, where, as defined in Appendix D,

$$D_n = kT_n\mu_n \quad (2.20)$$

and

$$D_n^T = \left[\frac{\mu_n n (V_n + S_n T_n)}{T_n} \right] \quad (2.21)$$

It is important to note from Eqs. 2.19a and b that the ξ'_n , electron effective force field, and ξ , the electrostatic field, play the same role in electron transport, where the electron effective force field is seen to be defined by

$$\xi'_n = - \left(\frac{d\chi}{dx} + kT_n \frac{d \ln N_C}{dx} \right) \quad (2.22)$$

This quantity ξ'_n arises from changes in electron affinity χ and from changes in conduction band effective density of states N_C with position. The quantity ξ arises, of course, from electric charge density. This realization of the identical roles played by ξ'_n and ξ in causing electron drift currents is very important to the understanding of photovoltaic action.²⁶ From the perspective of Eq. 2.19, the electron conventional current density J_n can be viewed as resulting from thermal diffusion, diffusion, and drift, with the latter arising from a total force on an electron given by

$$F_e = -e \left(\xi - \frac{d\chi}{dx} - kT_n \frac{d \ln N_C}{dx} \right) \quad (2.23)$$

The Eq. 2.19 formulations are seen to reduce to the usual³

$$J_n = e\mu_n n\xi + eD_n \frac{dn}{dx} \quad (2.24)$$

if the material does not have a varying electron affinity χ or varying conduction band effective density of states N_C and if there is no electron temperature gradient. As discussed in Chapters 4–7, in solar cell structures there often are abruptly stepped or graded material regions and abruptly stepped or graded heterojunctions. In those cases, the models for J_n given by Eqs. 2.19a and b are required to capture the device physics. As noted earlier, although valid for single-crystal or amorphous regions, the equations of this section can also work well for inorganic and organic multicrystalline and microcrystalline solids by accounting for the interface transport or by using effective mobilities. We will use Eq. 2.19 in our device analyses in Chapters 4–7 but assume the electron temperature can be characterized with a system temperature T having negligible variation with position.

2.3.1.2 BULK REGION VALENCE BAND TRANSPORT

The general expression for $p(x)$, the free hole population per volume in the valence band at some point in a material system, which is valid even when out of TE, is given by

$$p = \int_{-\infty_C}^{E_V} \left[\frac{1 + \exp - (E - E_{Fp})}{kT_p} \right]^{-1} A_V (E_V - E)^{1/2} dE \quad (2.25)$$

In this expression, E_{Fp} is the spatially varying hole quasi-Fermi level, T_p is the spatially varying hole temperature, and $A_V(E_V - E)^{1/2}$ is a model for the valence band density of states and its prefactor may vary with position. This parabolic model for the valence band density of states is rigorously valid for crystalline and polycrystalline materials and works well for amorphous inorganics, too. A Gaussian distribution can be utilized instead for organics. Eq. 2.25 may be simplified to

$$p = N_V \exp \left[\frac{-(E_{Fp} - E_V)}{kT_p} \right] = N_V \exp \left[\frac{-V_p}{kT_p} \right] \quad (2.26)$$

if the hole quasi-Fermi level E_{Fp} lies at least several kT_p above E_V . In Eq. 2.26, N_V is the valence band effective density of states and the quantity V_p locates the hole quasi-Fermi level with respect to E_V (see Appendix D). When the criterion for the use of Eq. 2.26 is fulfilled, the implication is that Boltzmann statistics are valid for determining the valence band population.

The results from Appendix D for the conventional current density J_p for holes are analogous to those obtained for the free electrons of the conduction band. To be specific, in the presence of a spatially varying hole quasi-Fermi level E_{Fp} and spatially varying hole temperature T_p , the hole conventional current density J_p can be written as

$$J_p = e\mu_p p \frac{dE_{Fp}}{dx} - e\mu_p S_p \frac{dT_p}{dx} \quad (2.27)$$

where the material parameters μ_p and S_p are the hole mobility and Seebeck coefficient, respectively. Equation 2.27 includes both hole drift and diffusion. To show this explicitly, Eq. 2.27 is rewritten in Appendix D as

$$J_p = e\mu_p p \left(\xi - \frac{d(\chi + E_G)}{dx} + kT_p \frac{d \ln N_V}{dx} \right) - eD_p \frac{dp}{dx} - eD_p^T \frac{dT_p}{dx} \quad (2.28a)$$

or alternatively as

$$J_p = e\mu_p p \xi + e\mu_p p \xi'_p - eD_p \frac{dp}{dx} - eD_p^T \frac{dT_p}{dx} \quad (2.28b)$$

Equations 2.28a and b use the parabolic density of states model but have equivalent forms for other density of states models. The hole diffusion coefficient D_p and the hole thermal diffusion coefficient (or Soret coefficient) D_p^T have been introduced into Eqs. 2.28a and b where, as defined in Appendix D,

$$D_p = kT_p \mu_p \quad (2.29)$$

and

$$D_p^T = \left[\frac{\mu_p p (S_p T_p - V_p)}{T_p} \right] \quad (2.30)$$

In Eqs. 2.28a and b the quantity ξ is the electrostatic field but ξ'_p is seen to be the hole effective force field defined by

$$\xi'_p = - \left(\frac{d(\chi + E_G)}{dx} \right) - kT_p \frac{d \ln N_V}{dx} \quad (2.31)$$

The hole effective force field ξ'_p arises from changes in hole affinity $\chi + E_G$ and from changes in valence band effective density of states N_v , as discussed in detail in Appendix D. It is important to note from Eqs. 2.28a and b that the ξ'_p , hole effective force field, and ξ , the electrostatic force field, play the same role in hole transport.²⁶ From the perspective of Eq. 2.28, the hole conventional current density J_p can be viewed as resulting from thermal diffusion, diffusion, and drift, with the latter arising from a total hole force given by

$$F_h = e \left(\xi - \frac{d(\chi + E_G)}{dx} + kT_p \frac{d \ln N_v}{dx} \right) \quad (2.32)$$

Interestingly, it can be seen from a comparison of Eqs. 2.22 and 2.31 that the electron and hole effective force fields can be very different. It can also be seen from Eqs. 2.19b and 2.28b that the electrostatic field causes the electron and hole conventional currents to flow in the same direction, which means it causes electrons and holes to move in opposite directions. Comparison of these same two equations further shows that properly designed changes in electron affinity and band density of states and hole affinity and band density of states can also cause electrons and holes to move in opposite directions. Put succinctly, both the electric field and effective fields can be used to break symmetry in a solar cell structure. Both are equally able to give rise to photovoltaic action.²⁶ This is a very important point. If one is willing to accept that electrostatic and effective fields need not both be present in a cell and to generalize these ideas to all sorts of solar cell structures, from p-n homojunctions to dye-sensitized solar cells, then a very general picture of photovoltaic action emerges: electrostatic fields, effective fields, or both may be used to break symmetry and to give rise to photovoltaic action. This perspective is the path we follow in this book.

The expressions of Eq. 2.24 are seen to reduce to the usual³

$$J_p = e\mu_p p \xi - eD_p \frac{dp}{dx} \quad (2.33)$$

if the material does not have a varying hole affinity $\chi + E_G$ or varying valence band effective density of states N_v and if there is no hole temperature gradient. As we will see, there often are graded material

regions and graded heterojunctions in solar cell structures, necessitating the use of Eq. 2.28 to capture all the device physics taking place. Although valid for single-crystal or amorphous regions, the hole transport equations of this section can also work well for inorganic and organic multicrystalline and microcrystalline solids by accounting for the interface transport or by using effective mobilities. We will use Eq. 2.28 in our device analyses in Chapters 4–7 but henceforth assume there is one temperature T for electrons and holes and its variation with position is negligible.

2.3.1.3 AMORPHOUS MATERIALS

Transport in amorphous solids is complex because current can be carried not only by electrons and holes in the conduction and valence bands, respectively, but also by carriers in gap states; i.e., the gap states may be of a high enough density that they too can support transport in some amorphous materials. To acknowledge this, the current density J must be written, in general, as

$$J = J_n + J_p + \sum_i J_{Gi} \quad (2.34)$$

Here J_n is the conduction-band contribution (from the delocalized states above the mobility gap in Fig. 2.10), J_p is the valence-band contribution (from delocalized states below the mobility gap in Fig. 2.10), and J_{Gi} is the current density from the i th group of gap states. In the case of J_{Gi} , the motion of electrons in gap states may often be best described in terms of their hopping from one site to another. Hopping involves tunneling, but, since these sites may not all be at the same energy, hopping is a phonon-assisted tunneling process. Every time the localized electron moves, it may emit or absorb a phonon. This makes hopping a thermally activated process and causes the mobility μ_G to be of the form

$$\mu_{Gi} = \mu_{Gi0} e^{-W(E)/kT} \quad (2.35)$$

where the quantity W is the activation energy.^{27,28} Since the mobilities of the delocalized states are expected to be orders of magnitude larger than those of localized states (the mobility gap), and since, among the localized states, mobilities can vary by orders of magnitude due to the $e^{-W(E)/kT}$

factor, the conductivity of amorphous materials can be tremendously affected by shifts in populations. For example, if light appreciably shifts the carrier population into localized states with large hopping mobilities or into band states, then large changes in the conductivity will result, and, in fact because of this, many amorphous semiconductors, both organic and inorganic, are strong photoconductors.

2.3.2 Transport processes at interfaces

There are a number of processes unique to interfaces that can allow carriers to cross the boundary between two materials or between two grains. These processes are in series with the bulk transport mechanisms just discussed. In this section we focus on these interface transport mechanisms. A metal-semiconductor structure in forward bias is used in Figure 2.19 to illustrate them. From the figure it is seen that mechanisms a to e involve the semiconductor majority carriers, while mechanism f involves both majority and minority carriers. Mechanism g involves only minority carriers. Although here we discuss these mechanisms in the context of a metal-semiconductor contact, the general features of these various interface transport mechanisms will also be found at other interfaces.

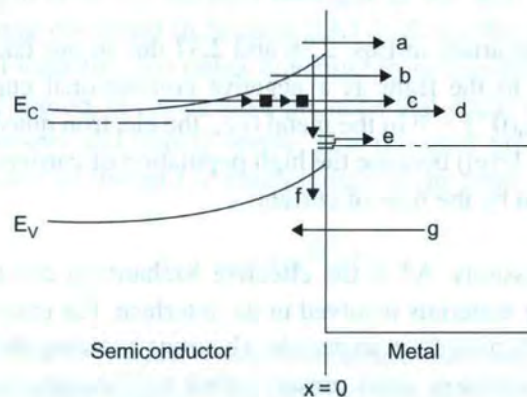


FIGURE 2.19 Interface transport mechanisms illustrated using a forward-biased, metal-semiconductor junction. Path a is thermionic emission, path b is thermally enhanced field emission, path c is multistep tunneling, path d is field emission, path e involves trapping and subsequent emission, path f is interface recombination, and path g is minority-carrier injection.

2.3.2.1 THERMIONIC EMISSION

Thermionic emission is a classical process (no tunneling) by which a carrier transfers from an allowed state in one material to an allowed state in another material with ideally no change in total energy. The general model, valid for semiconductor-semiconductor or metal-semiconductor interfaces, for the net current density J_{OB} coming over the barrier at an interface, may be written for electrons, for example, as.²⁹

$$J_{OB} = -A^* T^2 e^{-\phi_B/kT} [e^{E_{Fn}(0^-)/kT} - e^{E_{Fn}(0^+)/kT}] \quad (2.36)$$

Here ϕ_B is the barrier height, $E_{Fn}(0^-)$ is the shift in the quasi-Fermi level position at $x = 0^-$, and $E_{Fn}(0^+)$ is the shift in the quasi-Fermi level position at $x = 0^+$ with current flowing. These are measured positively up from the Fermi level TE position at the interface. This expression once again shows the current-driving role of quasi-Fermi levels first seen in Eqs. 2.18 and 2.27.

In the case of our example interface, the metal-semiconductor structure of Figure 2.19, this mathematical model for path a may be expressed as

$$J_{OB} = -A^* T^2 e^{-\phi_B/kT} [e^{V/kT} - 1] \quad (2.37)$$

The minus sign arises in Eqs. 2.36 and 2.37 due to our taking net electron emission to the right as a negative conventional current. In this expression, $E_{Fn}(0^+) = 0$ in the metal (i.e., the electron quasi-Fermi level is at the Fermi level) because the high population of carriers in the metal is not disturbed by the flow of current.

In these expressions, A^* is the effective Richardson constant³⁰; it is a function of the materials involved in the interface. For example, in crystalline and polycrystalline materials, electrons crossing the interface in conservative processes must preserve their total energy as well as the component of their $\mathbf{k}$ -vector that lies in the plane of the junction. The number of electrons in a materials system that are able to do this will depend on the $E = E(\mathbf{k})$ functions of the materials involved, and this

is reflected in the value of A^* . There can be materials systems where electrons must interact with phonons to adjust their $\mathbf{k}$ -vectors so they can fit into the $E = E(\mathbf{k})$ of their new host. In so doing, their energy is changed. For amorphous materials, this $\mathbf{k}$ conservation is relaxed, since $\mathbf{k}$ is not a “good quantum number.” The effective A^* must incorporate these variations from materials system to materials system.^{29,30}

2.3.2.2 THERMALLY ENHANCED FIELD EMISSION

Process b of Figure 2.19 is thermally enhanced field emission or thermionic field emission. Thermally enhanced field emission is a direct tunneling process by which an electron is transferred from an allowed state in one material to an allowed state in another. It differs from field emission, which is also a direct tunneling process, in that field emission (path d) is not thermally assisted.³⁰ Except for the higher semiconductor doping levels and lower temperatures, thermionic field emission is not expected to dominate over the parallel path of thermionic emission at semiconductor-metal interfaces.³⁰

2.3.2.3 MULTISTEP TUNNELING

Process c of Figure 2.19 is referred to as multistep tunneling. Such processes are what is termed indirect tunneling and may or may not be conservative, although the particular example shown is. Multistep tunneling may be thought of as the interface analogue of the bulk transport process of hopping discussed in Section 2.3.1.3. Since this path does not involve direct tunneling but rather tunneling from one defect to another in the barrier region, it can involve phonons and occur for a range of barrier thicknesses and doping levels. This transport process has been proposed to have a forward J-V characteristic of the form

$$J_{MS} = -J_0 e^{BT} e^{AV} \quad (2.38)$$

where A and B are constants.³¹ Here V is the band-bending change in the semiconductor barrier region for the forward bias direction. The quantity $J_0 e^{BT}$ multiplying the voltage term in Eq. 2.38 is seen to give, when plotted versus T, linear dependence on T. This is quite different from the temperature-activated forms of the voltage independent terms in Eqs. 2.36 and 2.37.

2.3.2.4 FIELD EMISSION

Process d of Figure 2.19 is pure field emission; i.e., direct tunneling through the semiconductor barrier by majority carriers from the bottom of the band. The field emission current density J_{FE} has a very strong dependence on any changes that take place in the semiconductor band bending, since this modifies the barrier shape and therefore the tunneling probability. Since path d necessitates direct tunneling through the semiconductor barrier at its widest, it is appreciable only for very high doping levels.³⁰

2.3.2.5 TRAPPING AND SUBSEQUENT EMISSION

Path e requires that an electron in the conduction band at $x = 0$ in our example interface of Figure 2.19 be trapped by a localized state at or near the interface and then be subsequently emitted into the metal. In general, such processes depend on the population of carriers in the initial states, on the population of carriers in the intermediary states, and on the population of carriers in the final states, as well as on capture cross-sections.

2.3.2.6 INTERFACE RECOMBINATION

Path f of Figure 2.19 is trap-assisted interface recombination. The current density J_{IR} flowing in the conduction band at $x = 0^-$ due to this process is obtained by recasting Eq. 2.9 into the form

$$J_{IR} = \frac{ev\sigma_n\sigma_p N_I [n(0^-)p(0^-) - n_i^2]}{\sigma_p [p(0^-) + p_1] + \sigma_n [n(0^-) + n_1]} \quad (2.39)$$

In this expression N_I is the density, per area of interface, of the trap states at energy E . If there is a distribution of gap states at an interface, then this expression must be summed over this distribution.

2.3.2.7 MINORITY CARRIER INJECTION

Process g seen in the forward-biased metal-semiconductor interface of Figure 2.19 is minority carrier injection. In the case of this figure, holes are generated in the valence band (by electrons moving to the right into the metal) at the metallurgical junction $x = 0$. These holes supply path f and any remaining holes move to the left into the bulk of the semiconductor by drift and diffusion. In many interfaces similar to our example,

path g is able to provide as many holes as are required by path f and by the bulk. In such a situation, the quasi-Fermi level for holes $E_{Fp}(0^-)$ must equal $E_{Fp}(0^+)$. If path g were not able to supply the holes required by path f and the bulk, then $E_{Fp}(0^-)$ would lie above $E_{Fp}(0^+)$ in energy.

2.3.2.8 THE SURFACE RECOMBINATION SPEED MODEL

Often all these various transport possibilities at an interface are modeled by using the following two expressions,³ which are linear in the carrier population:

$$J_n(x) = \pm e S_n [n(x) - n_0(x)] \quad (2.40a)$$

and

$$J_p(x) = \pm e S_p [p(x) - p_0(x)] \quad (2.40b)$$

The $n_0(x)$ and $p_0(x)$ in these expressions are the TE values of the free carrier populations at point x which is just to the right (interface to the left) or left (interface to the right) of the interface. The parameters S_n and S_p characterize this interface and are called surface recombination speeds. The sign choices seen in these equations depend on whether the interface is to the left or right of x as seen in Figure 5.20.

Equation 2.37 can be rigorously put into this form by rewriting it as

$$J_{OB} = -A^* T^2 e^{-\phi_B/kT} \frac{N_C}{N_C} (e^{V/kT} - 1) = -\frac{A^* T^2}{N_C} (n - n_0) \quad (2.40c)$$

which can be used to show that a surface recombination speed of $\sim 10^7$ cm/s adequately represents thermionic emission. Equation 2.39 can be put into the form of Eq. 2.40 as well by using the linearization assumptions discussed in Section 2.2.5.1.

2.3.2.9 GENERAL COMMENT

Figure 2.20 shows a very general solar cell structure in which electrons collected from the right contact (cathode) traverse the external circuit and do

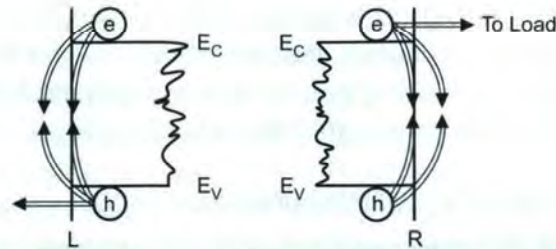


FIGURE 2.20 Contacts to a very general solar cell structure. Electrons that survive the loss mechanisms at R, all of which are due to holes at contact R, go off to the external circuit to do work at the load. Holes are collected at interface L in numbers that match electrons arriving from the load. The electrons at contact L are the source of loss there. In the surface recombination picture of Eq. 2.40, S_n characterizes the three electron paths and S_p the two hole paths for the right contact. An S_n used in Eq. 2.40 characterizes the two electron paths and an S_p the three hole paths for the left contact.

work at the load when the device is in the power quadrant. The number of electrons available for work in the external circuit is equal to the total number of arriving electrons at this cathode minus the arriving electrons lost to holes, as seen in the figure. Since some of the electrons recombine with holes at the contact surface or are thermionically emitted and then annihilated by holes—or suffer some other loss mechanism at the contact—we always need to calculate the total J_n and J_p at the contact to get the net J that flows through the external circuit. As seen from Figure 2.20, the algebraic sum of $J_n + J_p$ evaluated at R subtracts out the electrons lost to holes and gives the number of electrons entering the external circuit. The analogous situation happens for holes at contact L (the anode). The number available to meet the electrons arriving from the load is equal to the arriving hole number minus those lost to electrons at L. Of course, the solar cell must arrange its carrier populations, electric field distribution and current flows in steady state to make sure all of this happens.

2.3.3 Continuity concept

The continuity concept is a very powerful part of our device physics toolbox. It is accounting applied to electrons and holes. For example, considering free electrons first, the free electron conventional current density $J_n(x_1)$ at some point x_1 and the free electron conventional current density at some point x_2 (where $x_2 > x_1$) must be equal in steady state unless free electrons are (1) gained by photogeneration or (2) lost

to net recombination in the region x_1 to x_2 . Expressed mathematically, this means

$$\frac{J_n(x_1)}{e} = \frac{J_n(x_2)}{e} + \int_{x_1}^{x_2} \int_{\lambda} G_{ph}(\lambda, x) dx d\lambda - \int_{x_1}^{x_2} (\mathcal{R}^R + \mathcal{R}^L + \mathcal{R}^A) dx \quad (2.41)$$

where the necessity of converting conventional electron current density J_n into electron particle density $-J_n/e$ has been taken into consideration. The definitions of Section 2.2.5 and Section 2.2.6 have been used in Eq. 2.41. This equation is the steady-state integral form of the continuity concept for free electrons. If we wanted the general time-dependent version, we would have to add a term accounting for the possible build-up of electrons in the region x_1 to x_2 and terms accounting free electrons arising from trapping and de-trapping traffic into and out of the conduction band. Fortunately, we are generally interested in steady-state behavior in solar cells. Equation 2.41 can also be expressed in a steady-state differential form:

$$\frac{\partial J_n / \partial x}{e} = - \int_{\lambda} G_{ph}(\lambda, x) d\lambda + \mathcal{R}^R + \mathcal{R}^L + \mathcal{R}^A \quad (2.42)$$

The continuity concept applied to free holes in the valence band for the same region x_1 to x_2 gives

$$\frac{J_p(x_2)}{e} = \frac{J_p(x_1)}{e} + \int_{x_1}^{x_2} \int_{\lambda} G_{ph}(\lambda, x) dx d\lambda - \int_{x_1}^{x_2} (\mathcal{R}^R + \mathcal{R}^L + \mathcal{R}^A) dx \quad (2.43)$$

The definitions of Section 2.2.5 and Section 2.2.6 have again been used. This equation is the steady-state integral form of the continuity concept for holes. If we wanted the general time-dependent version, we would have to add a term accounting for the build-up of holes in the region x_1 to x_2 and a term accounting for free holes arising from trapping and detrapping. Equation 2.43 can also be expressed in differential form:

$$\frac{\partial J_p / \partial x}{e} = \int_{\lambda} G_{ph}(\lambda, x) d\lambda - (\mathcal{R}^R + \mathcal{R}^L + \mathcal{R}^A) \quad (2.44)$$

2.3.4 Electrostatics

A solar cell has a lot of things going on inside: generation, recombination, currents flowing, and perhaps trapped charge. As demonstrated by Eqs. 2.19 and 2.28, effective fields and the electric field in the cell are involved in the current flow. The electric field is in turn modified by the currents flowing and the charge in the delocalized states, traps and recombination centers. All of this activity is included in Poisson's equation, which may be written as

$$\frac{\partial(\epsilon\xi)}{\partial x} = e \left[p - n + \sum p_T - \sum n_T + N_D^+ - N_A^- \right] \quad (2.45)$$

where ϵ is the permittivity, which may be a function of position. The right-hand side of this equation is called the space charge or the charge density. The terms in the large parentheses in Eq. 2.45 account for the charge per volume due to free carriers and for charge per volume in localized states (dopants, recombination centers, and traps). As seen, the two summations used in the expression are needed to account for all the positive charge and all the negative charge in defect gap (recombination centers and traps) states at different energies in the gap. As also seen, dopants are treated separately since they are purposefully introduced. One donor and one acceptor dopant level have been used for definitiveness.

2.4 THE MATHEMATICAL SYSTEM

Collecting all our previous work, we can now write down the full mathematical system that describes all the physics taking place in a solar cell in steady state. This mathematical system is made up of, unfortunately, a large set of coupled, non-linear equations. This set includes Eqs. 2.19 and 2.28, the equations of Section 2.2.5, the continuity equations for electrons and holes, and Poisson's equation. The solution to this set for n , p , J_n , J_p , etc., must be consistent with the boundary conditions imposed by the interface transport discussed in Section 2.3.2. We have to obtain this solution in order to establish the cell's current density-voltage (J-V) characteristic (see Fig. 1.3), which is required for cell evaluation, design, and optimization. Since we have been staying with one dimension, this total conventional current density J of the J-V characteristic is a constant and is obtained from

$$J = J_n + J_p \quad (2.46)$$

where the components J_n and J_p are evaluated at the same plane (any plane) in the cell. The terminal voltage V produced by the cell at some operating point while delivering the current density J is given by the integral over the structure of the difference between the electric field distribution present at the selected operating point $\xi(x)$ and the electric field distribution present in TE which we term $\xi_0(x)$; i.e.,

$$V = \int_{\text{structure}} [\xi(x) - \xi_0(x)] dx \quad (2.47)$$

It must be stressed that this expression is valid regardless of whether the cell has an exciton-producing absorber or free electron-hole-producing absorber or is any cell structure from a dye sensitized solar cell to a conventional p-n junction device. Put succinctly, it is valid for all types of cells. Equation 2.47 is of such general validity because it calculates the relative shift of the contact Fermi levels present at the selected operating point. This shift is the voltage V at this operating point. The sign convention assumed in writing Eq. 2.47 is that the cathode is the left-hand contact.

As we will see, establishing the current densities J_n and J_p —and therefore the J-V characteristic—for a solar cell can be done analytically in some situations, with the help of assumptions. We will explore this approach in Chapters 4–7. However, turning a computer loose to tackle the full mathematical system, and not making any of those assumptions, is very powerful and insightful and we will do that too in Chapters 4–7. In the computer analysis, we will make extensive use of numerical solutions to the full mathematical system. In this numerical modeling, the specific versions of the equations of the mathematical system that will be utilized are the following:

$$J_n = e\mu_n n \left(\xi - \frac{d\chi}{dx} - kT \frac{d \ln N_C}{dx} \right) + eD_n \frac{dn}{dx} \quad (2.48a)$$

$$J_p = e\mu_p p \left(\xi - \frac{d(\chi + E_G)}{dx} + kT \frac{d \ln N_V}{dx} \right) - eD_p \frac{dp}{dx} \quad (2.48b)$$

$$\frac{\partial J_n / \partial x}{e} = - \int_{\lambda} G_{ph}(\lambda, x) d\lambda + \mathcal{R} \quad (2.48c)$$

$$\frac{\partial J_p / \partial x}{e} = \int_{\lambda} G_{ph}(\lambda, x) d\lambda - \mathcal{R} \quad (2.48d)$$

$$\frac{\partial(\epsilon\xi)}{\partial x} = e(p - n + \sum p_T - \sum n_T + N_D^+ - N_A^-) \quad (2.48e)$$

In these equations, $\mathcal{R}$ can be any of the unimolecular or bimolecular recombination mechanisms of Section 2.2.5. In our numerical modeling we employ the full non-linearized formulations discussed in Section 2.2.5 for whichever $\mathcal{R}$ is assumed. For example, we will often assume $\mathcal{R}$ is controlled by S-R-H recombination and use

$$\mathcal{R}^L = \frac{v\sigma_n\sigma_p N_T(np - n_i^2)}{\sigma_p(p + p_1) + \sigma_n(n + n_1)} \quad (2.48f)$$

summed over some gap state distribution. For Eq. 2.48e the trapped charges n_T and p_T at energy E as well as the ionized dopant concentrations N_A^- and N_D^+ are computed using Fermi-Dirac statistics, as discussed in Appendix C. As seen in that Appendix, these quantities become functions of n and p in steady state. Keeping that in mind, we see that set 2.48 has 5 equations and 5 unknowns.

The quantity $G_{ph}(\lambda, x)$ in this set is the photogeneration function of Section 2.2.6. In the case of free electron-hole pair-caused absorption, it is modeled in the numerical simulations by using $\alpha(\lambda)I_0(\lambda)e^{-\alpha(\lambda)x}$ (see Eq. 2.2); i.e., the absorption mechanism is taken to follow the Beer-Lambert law. In the case of exciton-caused absorption, $G_{ph}(\lambda, x)$ is modeled by a delta-function-like distributions at the region of exciton dissociation. This point is discussed further in Chapter 5.

In the numerical results presented in this text, the computer solves the equations subject to the boundary conditions

$$J_n(L) = eS_n [n(L) - n_0(L)] \quad (2.48g)$$

and

$$J_p(L) = -eS_p [p(L) - p_0(L)] \quad (2.48h)$$

for the left (L) contact to the cell structure and subject to the boundary conditions

$$J_n(R) = -eS_n [n(R) - n_0(R)] \quad (2.48i)$$

and

$$J_p(R) = eS_p [p(R) - p_0(R)] \quad (2.48j)$$

for the right (R) contact. These are taken from Eq. 2.40 and assume a coordinate system with x increasing from left to right. As we establish in Chapter 4, these boundary conditions can be made inconsequential by various layers we can place adjacent to contacts. By simultaneously solving this whole set of equations numerically, the computer then assembles the J-V characteristics for no illumination (dark J-V) and illumination (light J-V) situations in our discussions of Chapter 4–7. When the results are tied to the device coordinate system, the conventional current density is taken as positive when it flows in the positive x -direction of the device coordinates. Except where noted, voltage is taken as positive if the Fermi level of the right contact is above that of the left contact. In discussions tied to plots of J versus V , J is taken as negative in the power quadrant. The resulting numerical solutions give us the J-V behavior but also allow us to peer inside a cell as it is operating and thereby allow us to explore the roles of diffusion, electrostatic fields, effective fields, drift, recombination, trapping, interfaces, etc.

2.5 ORIGINS OF PHOTOVOLTAIC ACTION

As discussed earlier, Eqs. 2.19 and 2.28 give an understanding of what can make J occur in a solar cell. These equations show that the answer lies in (1) the presence of an electric field, (2) the presence of effective force fields (changes with position in affinities and band effective densities of states), (3) diffusion, and (4), if there is temperature gradient,

thermal diffusion. If we neglect temperature gradients, which can be set up under the presence of light, there are three possible causes of photovoltaic action. As discussed in Chapter 3, there really are only two important causes: the two terms in these equations that make one direction different than the other; i.e., the terms that tend to push electrons one way and holes the other, thereby separating carriers. These symmetry breaking terms are the electric field and effective force field terms.

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