

7 Amorphous Hydrogenated Silicon, a-Si:H

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7.1 Introduction

The research in the field of amorphous semiconductors, from the very beginning, has been driven by both the scientific interest in basic aspects of disorder in the properties of solids and technological applications. In the early years chalcogenide glasses were at the center of the interest owing to thin-film applications in imaging, xerography, memory and switching devices. At that time amorphous silicon and amorphous germanium, a-Si and a-Ge, were of more academic scientific interest. As simple elemental tetrahedrally bonded amorphous semiconductors, they served as model systems in which the disorder was less complicated, being defined not by chemical composition but by the structural disorder only. These amorphous semiconductors were prepared as thin films, about 0.1–1 μm thick, on glass or quartz substrates by a variety of methods such as thermal or e-gun evaporation, sputtering, ion bombardment and electrolysis. The simplest model for the structure of tetrahedrally bonded semiconductors is the continuous random network (CRN) structure in which the average coordination number is close to 4. Fluctuations in the bond angles and nearest-neighbor distances lead to a loss of long-range order even in the second-neighbor shell. This loss of long-range order is the characteristic structural feature of amorphous semiconductors. As a result, important theoretical concepts which are based on periodicity (Bloch's principle) fail, such as band structure, k -vector, Bloch states, effective masses and optical selection rules. The optical spectra of amorphous semiconductors appear to be more or less broadened versions of their crystalline counterparts, which shows that the density-of-states distribution is the decisive quantity; this is largely determined by the nature and structure of the chemical bonding. Perhaps the most obvious effect of disorder is the localization of electronic states, in particular near the band edges, which strongly affects the transport properties.

In the 1960s the major challenge consisted in understanding the role of disorder and in developing new theoretical concepts. However, the early forms of amorphous silicon had unacceptable electronic properties due to large defect densities, which caused high densities of states in the energy gap, which pinned the Fermi level. The only defect that has been identified microscopically by electron spin resonance is the Si dangling bond (Si-db), which is present in an amount of some 10^{19} cm^{-3} in evaporated or sputtered material.

Si dangling bonds form deep gap states, which act as effective centers for nonradiative recombination. The conductivity in this kind of amorphous silicon was very low and, below room temperature, was in general determined by hopping transport between localized gap states. Owing to the effective pinning of the Fermi level in a high density of gap states, the conductivity could not be varied by doping, illumination or carrier injection. Such material properties prevented this material from being useful for electronic devices.

The situation changed rather abruptly when the beneficial role of hydrogen incorporation was discovered at the beginning of the 1970s. Six main milestones in the material and device research led to a burst of research activities in this field and to numerous applications of hydrogenated amorphous silicon, a-Si:H:

- The first to use the plasma deposition technique were Chittick, Alexander and Sterling in 1969 [1]. In this technique, silane (SiH_4) was decomposed in a radio-frequency (rf) glow discharge and the film was formed on heated substrates.
- The work at the University of Dundee showed that the defect density in this kind of amorphous silicon was low, which resulted in high photoconductivity [2].
- The essential role of hydrogen in passivating defects was first discovered by the Harvard group, studying sputtered a-Si:H and a-Ge:H [3]. Later on, numerous studies gave proof that the superior semiconducting and photoelectric properties of glow-discharge-deposited amorphous silicon were due to the incorporation of hydrogen.
- In 1975 Spear and LeComber [4] reported on substitutional n-type and p-type doping by addition of phosphine or diborane to the process gas. This procedure allowed one to control the electrical conductivity over 10 orders of magnitude.
- The first report on photovoltaic devices, by Carlson and Wronski in 1976 [5], demonstrated the feasibility of a-Si:H solar cells.
- The research on displays started some years later, after the first report on the fabrication and physics of a thin-film transistor [6].

The preparation and properties of hydrogenated amorphous silicon have been described in numerous review articles and monographs (e.g. [7–11]), and the development is well documented in the proceedings of the biannual International Conference on Amorphous and Microcrystalline Semiconductors, which are published in regular issues of the *Journal of Non-Crystalline Solids*. Today hydrogenated amorphous silicon, a-Si:H, offers a mature material and device technology, used for solar cells, thin-film transistors, sensors, imaging, radiation detectors and displays. Among the various material choices for thin-film solar cells, this is the only technology which so far has been able to overcome the barrier to mass production of large-area modules and to occupy a reasonable share of the world market (about 10%).

7.2 Preparation and Structural Properties of Amorphous Silicon

Amorphous silicon cannot be made by rapid cooling of a Si melt. The amorphous material, instead, is prepared by deposition from the gas phase onto substrates which are held at temperatures far below the melting temperature. A large variety of techniques has been used: thermal evaporation, sputtering, chemical vapor deposition using silane (CVD), photo-CVD, plasma-enhanced chemical vapor deposition (PECVD), and thermo-catalytic hot-wire deposition (HWCVD). There are no differences in principle in the microstructures of amorphous films prepared by the various methods. The differences lie in the deposition rate and the kind and concentration of defects (dangling bonds and voids). PECVD has led to the lowest defect densities and, therefore, is widely used now in industrial applications.

Thermodynamically, amorphous silicon (a-Si) is in a metastable state. Although an ideal structure might be described by a random network structure, the real structure can be varied experimentally in many ways. Therefore the material properties strongly depend on the preparation conditions and on the thermal history of an amorphous sample. Thermal annealing has been shown to produce changes in practically all material properties (enthalpy, electrical properties, defect densities, optical properties, etc.) [12]. It has been found that the free energy of annealed a-Si (relaxed state) is about 0.11 eV/atom higher than that of crystalline silicon [13]. Heating above a temperature of about 500°C usually induces a transition into the thermodynamically more stable crystalline phase. The kinetics of solid phase crystallization (SPC) are characterized by nucleation and growth of crystal clusters at the expense of the surrounding amorphous material. Laser recrystallization of amorphous silicon has become an important technique for the fabrication of polycrystalline silicon thin-film transistors. Recently, SPC has attracted high interest as a result of the experience that the presence of certain metals strongly modifies the nucleation and growth process. Such techniques enable the engineering of polycrystalline silicon thin films at low temperatures for new device applications such as thin-film transistors or polycrystalline silicon thin-film solar cells. A particularly interesting example of this kind of processing is the creation of a polycrystalline silicon layer with a grain size of about 10 μm on a glass substrate by an Al-induced layer exchange process [14]. In this process, a film stack of glass/Al/a-Si is transformed by annealing at about 400°C into glass/poly-Si/Al(Si) such that after etching of the Al(Si) layer a polycrystalline silicon layer on glass remains, which may serve as a seeding layer in subsequent deposition processes.

In PECVD, silane (SiH_4) or mixtures of silane with rare gases or hydrogen are decomposed in a glow discharge. In most cases, parallel-plate systems in a stainless steel reactor have been used. The most important deposition parameters are substrate temperature, base pressure, flow rate of the process gas, power density and frequency. High-quality a-Si:H films are grown at de-

position rates of typically 0.1 nm/s at substrate temperatures in the range 150–250°C. The progress achieved by using this method is that the density of deep defects (Si dangling bonds) can be reduced to values of below 10^{16} cm^{-3} owing to the incorporation of hydrogen. The effect of hydrogen is to saturate dangling-bond defects and to lower the average coordination number, which allows the construction of a more relaxed disordered network. The hydrogen content can vary widely with the deposition conditions (5–40%). Infrared spectroscopy reveals various bonding configurations of hydrogen. In optimized films, the hydrogen concentration amounts to 5–15% and the density of neutral Si dangling bonds is less than 10^{16} cm^{-3} . The IR spectra of such films show that the hydrogen is bonded predominantly in an isolated Si-H configuration (absorption at 2000 cm^{-1}). However, NMR studies suggest that the hydrogen may be inhomogeneously distributed. Annealing of the films at temperatures above the deposition temperature leads to the evolution of hydrogen, which is accompanied by an enhancement of the defect density. In films deposited at around 250°C, the evolution rate peaks at 550°C, whereas films made at lower temperatures tend to show a second evolution peak near 350°C. The occurrence of this low-temperature peak points to the existence of a porous structure, which enables rapid hydrogen diffusion. Owing to the pronounced role of hydrogen, this kind of amorphous silicon may be considered rather as a hydrogen–silicon alloy. Practically all film properties depend on the hydrogen content [7–10].

A particular advantage of plasma deposition is a high flexibility in the choice of the process gases, which allows one to easily modify the properties of the deposited films. Variations of the deposition parameters have been found to result in higher deposition rates and modifications of the material. Doping can be achieved by adding controlled amounts of B_2H_6 or PH_3 to the process gas. Alloy films such as $\text{a-Si}_{1-x}\text{Ge}_x\text{:H}$ and $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ can be deposited from gas mixtures of SiH_4 with GeH_4 or CH_4 , respectively. These films allow one to tune the energy gap to lower or higher values by controlling the composition of the process gas. Strong hydrogen dilution of the process gas results in the formation of microcrystalline silicon films ($\mu\text{c-Si:H}$). The structural and electronic properties of such plasma-deposited films have been studied intensively over more than 20 years [7–11].

7.3 Electronic Properties of Hydrogenated Amorphous Silicon, a-Si:H

The electronic properties of the amorphous films depend sensitively on the density and energy distribution $N(E)$ of the localized gap states. In particular, these states determine the shape of the absorption edge, the doping efficiency, transport and recombination, as well as the widths of space charge layers in devices. Figure 7.1 displays schematically a model of $N(E)$, including both intrinsic and extrinsic defect states. Inside the bands, the density-of-

states (DOS) distributions of the valence and conduction bands of amorphous semiconductors differ only little from those of their crystalline counterparts. In the optical spectra, the main effect is a broadening of the spectra. The states inside the bands are considered to be delocalized but, of course, owing to the loss of long-range order, they are no longer Bloch states. An important effect of disorder is that closer to the band edges, the states become localized. The most widely applied model suggests that a transition from extended to localized states occurs at distinct energies E_C and E_V , where the carrier mobilities drop abruptly owing to the change in the character of the states [7, 11]. In an amorphous semiconductor, these mobility edges play a similar role to the band edges in crystalline materials.

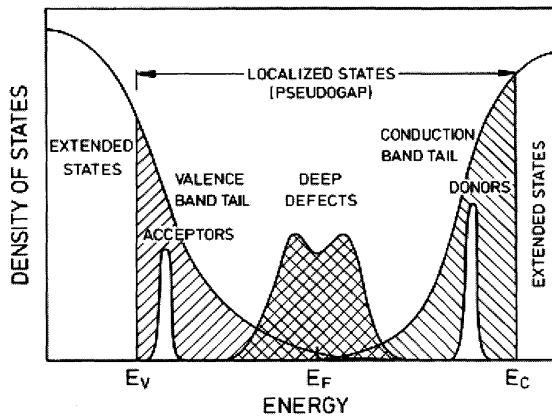


Fig. 7.1. Model of the density-of-states distribution in the energy gap of a-Si:H [11]

A characteristic of the DOS distribution in amorphous semiconductors is tails of localized states extending from both edges deep into the gap. These states are considered to arise from potential fluctuations due to disorder. In addition to these tail states, one expects deep states which originate from specific defects. Such defects may be formed in a random network structure in order to release internal stress but may also arise from unfavorable growth conditions. In a-Si:H the simplest deep defect is an unsaturated bond (Si-db), which has three differently charged states: unoccupied (positive, D^+), singly occupied (neutral, D^0) and doubly occupied (negative, D^-). In undoped a-Si:H the D^0 state is located around midgap, while the D^- state is higher in energy by the correlation energy of about 0.2 eV. Extrinsic states originate from impurities. These films contain hydrogen in a concentration of up to 15 at% and are strongly contaminated with oxygen, nitrogen and carbon in concentrations of the order of 10^{19} cm^{-3} . So far no gap states due to these impurities have been identified. The only known impurity states are those

that arise from substitutional doping by incorporation of elements from group III and V of the periodic table, forming flat donor or acceptor states.

The shape of the absorption edge reveals the general features of the DOS distribution (Fig. 7.2). A comparison of the absorption spectra of amorphous and crystalline silicon reveals a shift of the absorption edge of a-Si:H to higher energy and a strong enhancement of absorption in the visible range of the spectrum, which has often been related to the relaxation of the k -selection rule due to the loss of long-range order. This enhancement of absorption is the basis of important applications such as solar cells, and imaging and optical sensors. An optical gap may be defined in different ways. Rather often, E_{03} and E_{04} are used, which are the photon energies where $\alpha = 10^3 \text{ cm}^{-1}$ and 10^4 cm^{-1} , respectively. Another, more physical way is to use the concept of nondirect optical transitions, which takes into account the loss of the k -selection rule in a disordered structure by plotting the data as $(\alpha h\nu)^{1/2}$ versus $h\nu$ (Tauc plot). By extrapolating the straight line to the energy axis, values for the energy gap of about 1.75 eV are found. A justification for this procedure is that similar values have been obtained from the analysis of transport properties. However, one has to keep in mind that in this case the analysis yields a different quantity, namely the value of the mobility gap $E_C - E_V$. The value of the energy gap appears to be a unique function of the hydrogen concentration C_H in the film [8]. It amounts to 1.2–1.5 eV in evaporated or sputtered material with $C_H = 0$ and increases linearly with C_H in hydrogenated films (1.6–2.0 eV).

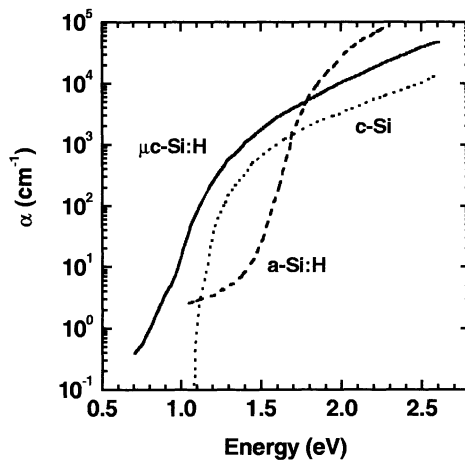


Fig. 7.2. Absorption edges of a-Si:H, monocrystalline Si and μ c-Si:H

Below $\alpha \approx 3 \times 10^3 \text{ cm}^{-1}$, the absorption constant decreases exponentially with energy; $\alpha \sim \exp[-(E/E_0)]$ (Urbach edge). The Urbach parameter E_0 depends on both temperature and the general disorder in the film. The Ur-

bach edge can be related to the exponential bandtails, and it is commonly believed that in a-Si:H the slope of the absorption edge is determined by the slope of the valence bandtail. The values of E_0 (50 meV) for films prepared under optimized conditions agree fairly well with the slope of the exponentially varying density of states of the valence bandtail derived from transport studies. The conduction bandtail is considerably steeper. Time-of-flight experiments have been consistently explained by a slope of about 25 meV [15].

At low photon energies, the absorption curve of a-Si:H levels off and a plateau develops, which is assigned to defect absorption. This defect-related absorption shoulder at low photon energies has quite frequently been used for quantitative defect analysis, applying techniques such as photocurrent spectroscopy and photothermal spectroscopy [16]. The value of α in this energy range is considered a figure of merit for the film quality. In undoped optimized films where, according to electron spin resonance, the concentration of neutral dangling bonds is about 10^{16} cm^{-3} , the value of α at 1.25 eV is in the order of 1 cm^{-1} .

The transport properties are strongly affected by disorder. In a-Si:H, where the density of gap states is low, transport is considered to take place predominantly in extended states above the mobility edges E_C and E_V . The carrier mobility cannot be determined experimentally as in crystalline silicon by the Hall effect, owing to the sign anomaly in amorphous semiconductors. The observation, the explanation of which is still one of the challenges in this research field, is that the sign of the Hall effect is opposite to that expected for the predominant carriers, e.g. positive for electrons. It is estimated that the mobility of the extended states is in the region of $10 \text{ cm}^2/\text{V s}$. Carriers in localized states can contribute to conduction with much lower mobility by thermally activated tunneling (hopping transport). If the density of states at the Fermi level is high, variable-range hopping may be observed, with a characteristic temperature dependence of the conductivity, $\ln \sigma \propto -(T_0/T)^{1/4}$ [7]. The existence of sharp mobility edges is still controversial and has been questioned as a result of consideration of electron-phonon coupling [11]. Although there is no direct proof for their existence, most experimental results are discussed in terms of this model.

A breakthrough in the physics of amorphous semiconductors was the discovery that a-Si:H can be effectively doped by adding controlled amounts of PH_3 or B_2H_6 to the process gas [4]. In an amorphous semiconductor, the donors deliver their electrons to empty states near the Fermi level. The resultant shift of the Fermi level, therefore, depends on the DOS distribution, and the doping effect in a-Si:H is closely related to the low density of defect states. Figure 7.3 displays typical results of doping. For P doping, the maximum conductivity at 300 K, σ_{RT} , of about $10^{-2} \text{ S cm}^{-1}$, is attained at a concentration of 10^3 – 10^4 ppm PH_3 in the gas phase. At higher doping levels σ_{RT} decreases, presumably owing to the generation of additional defects. For B doping, σ_{RT} decreases at low doping levels, and attains at a high doping level a maxi-

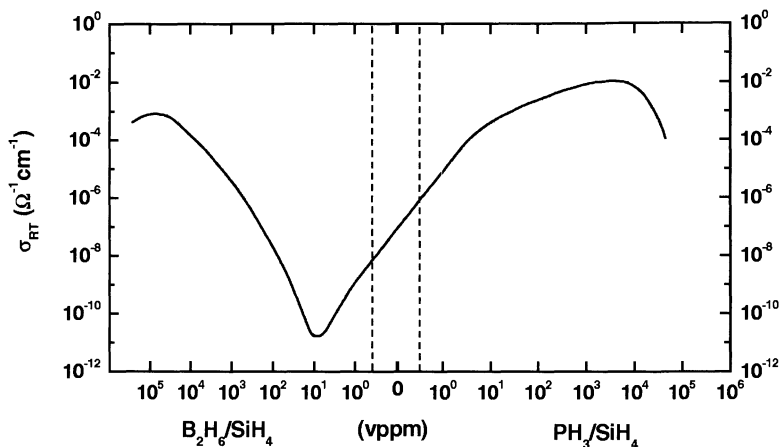


Fig. 7.3. Electrical conductivity at 300 K as a function of the doping level in the gas phase (see e.g. [4, 10, 11])

mum close to $10^{-3} \text{ S cm}^{-1}$. At the minimum, the Fermi level crosses midgap, $E_C - E_F = (1/2)(E_C - E_V)$, and the type of conduction changes from n- to p-type. Using $\sigma_{RT} \approx 10^{-12} \text{ S cm}^{-1}$, the value of the mobility gap can be estimated as 1.7 eV at 300 K. Whereas at high doping levels the results from different laboratories agree fairly well, there are pronounced differences at low doping levels. This is an expression of the influence of the specific deposition conditions on the concentration of deep defects. The details of the doping mechanism have turned out to be very complicated, involving reactions with dangling bonds and hydrogen. Experiments show that the concentration of defects increases strongly with doping, and both the density and the energy position of the defect states are essentially controlled by the position of the Fermi level. This points to a very general defect creation mechanism [16, 17].

7.4 Photoluminescence and Photoconductivity

At temperatures below of 50 K, optimized undoped a-Si:H exhibits photoluminescence (PL) with a quantum efficiency close to unity [18]. The emitted spectrum consists of a single structureless band centered at 1.3–1.4 eV with a width ΔE_{FWHM} of 0.25–0.3 eV (Fig. 7.4). In defect-rich and doped films the emission is quenched and additional structure appears at 0.8–0.9 eV, shown in Fig. 7.4 for the case of boron-doped films. Although the detailed nature of the intrinsic and defect-related emissions is still a matter of debate, it is most widely believed that the intrinsic process occurs by radiative tunneling of electrons and holes localized in the respective bandtails. The photoconductivity (PC) and the photoluminescence show anticorrelated temperature depen-

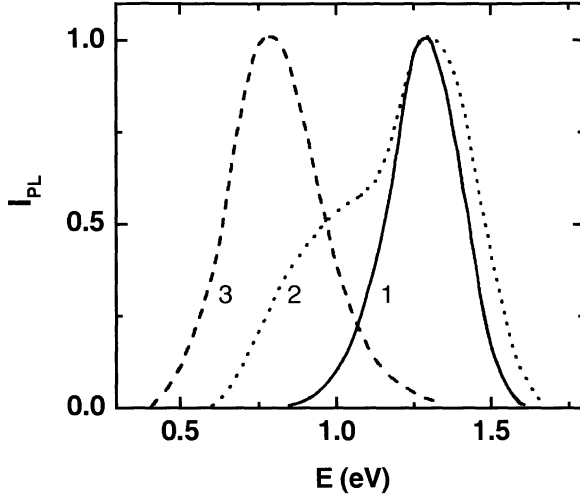


Fig. 7.4. Photoluminescence spectra (normalized intensity I_{PL}) showing the intrinsic emission band at 1.4 eV of undoped a-Si:H (1) and the defect-related band at 0.8 eV of a-Si:H doped with 100 ppm (2) and 1000 ppm (3) of boron

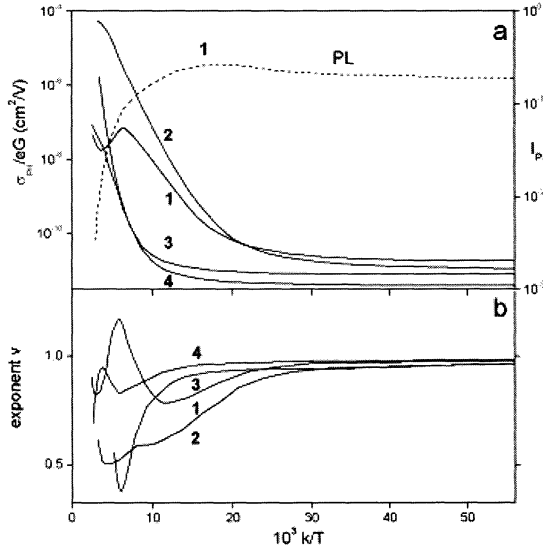


Fig. 7.5. Temperature dependence of **a** the PL intensity I_{PL} and the normalized photoconductivity $\sigma_{PH}/eG = \mu\tau$ at $G = 3 \times 10^{20} \text{ cm}^{-3} \text{ s}^{-1}$ ($\lambda = 525 \text{ nm}$) and of **b** the exponent ν of the intensity dependence $\sigma_{PH} \propto G^\nu$. PECVD a-Si:H: (1) undoped, (2) doped 100 ppm PH_3 , (3) doped 10^3 ppm B_2H_6 , (4) sputtered a-Si:H (undoped) [19]

dences [19]. Whereas, with rising temperature, the PL intensity is quenched, the photoconductivity increases (Fig. 7.5). This behavior suggests that we should distinguish two temperature ranges of different behavior:

- At $T < 60$ K, the PL quantum efficiency is large (close to unity in good films) and independent of temperature. The photoconductivity σ_{PH} is very small and varies linearly with the light intensity G . Its magnitude normalized by the charge e and generation rate G , $\sigma_{\text{PH}}/eG = \mu\tau$, is about 10^{-11} cm²/V and varies only very little with the quality of the sample. In Fig. 7.5a the product $\mu\tau$ varies only by a factor of 5, whereas the defect densities in the films differ by many orders of magnitude. This transport is quite generally assigned to tunneling of carriers between localized states in the bandtails.
- At $T > 60$ K, the PL intensity is quenched, and σ_{PH}/eG increases strongly. In this temperature range the magnitude of $\sigma_{\text{PH}}(G, T)$ and the kinetics are determined in a complicated way by the defect density, Fermi-level position and other factors. This can be seen from the complicated temperature dependence of the exponent in Fig. 7.5b. Here, transport occurs in extended states above the mobility edges, and Si dangling bonds are considered to be the primary centers for nonradiative recombination [20]. An important feature of phototransport in this regime is that σ_{PH} is tremendously enhanced when the Fermi level is shifted from midgap towards the mobility edges. This effect is particularly pronounced for n-type films when $E_{\text{C}} - E_{\text{F}}$ moves from 0.8 to 0.4 eV. For P-doped samples the mobility–lifetime product $(\mu\tau)_{\text{n}}$ can reach values of up to 10^{-4} cm²/V [19].

7.5 Metastable States

It is a characteristic property of hydrogenated amorphous semiconductors, of which a-Si:H is representative, that deep defects are created by the breaking of weak bonds when band tail states are populated. This can be achieved by exposure to light, carrier injection, strong accumulation in the conduction channel of an a-Si:H thin-film field effect transistor and doping (see above). It has also been reported that defects are generated at elevated temperatures ($T > 420$ K) in thermal equilibrium with the occupancy of tail states [10]. Some of these defects can be frozen in by quenching the film to $T < 420$ K. Such instabilities appear to be an inherent feature of the amorphous structure. The DOS distribution shown in Fig. 7.1 thus is not stable but varies with temperature, doping level and light absorption and during the operation of devices. Most electronic properties therefore depend to some extent on sample history and treatment.

In undoped a-Si:H films of device quality, light exposure causes a reversible decrease of both the dark conductivity and the photoconductivity, indicating a shift of the Fermi energy towards midgap and a decrease of the recombination lifetime [21]. These light-induced changes can be annealed completely at

temperatures of around 170°C. The reason for this Staebler–Wronski effect is a light-induced enhancement of the density of Si dangling bonds to values of typically 10^{17} cm^{-3} . The microscopic mechanism of defect creation is still one of the most important open questions in this research field. Apparently the defect creation is linked not to the absorption process (photodegradation) but to some secondary effect which involves nonequilibrium carriers. This effect could be either recombination or capture of carriers into localized states. It is widely believed now that in device quality material, the effect is intrinsic to hydrogenated films, being the result of disorder and the presence of hydrogen. Most of the results are in accordance with a model where recombination at weak bonds results in bond breaking. The broken bonds are considered to be stabilized by a mechanism which involves the motion of hydrogen atoms. This interpretation is supported in particular by the observation that films deposited by the hot-wire technique are more stable and have a much lower hydrogen content than a-Si:H made by PECVD. Such a participation of hydrogen in the mechanism of defect creation should lead to a spatial correlation between dangling bonds and neighboring SiH bonds, which, however, has not been observed in magnetic resonance studies. Research is being directed towards minimizing the metastability by a proper control of the deposition conditions influencing the microstructure and the concentration of weak bonds (steeper bandtails). There are conflicting observations about deuterated material, a-Si:D, which has been reported to be more stable. It is unclear whether this is due to slower degradation involving SiD bonds or whether this arises from a change in the microstructure of the samples investigated. Some results suggest that the microstructure of the films might indeed be an important factor. Heavy-hydrogen dilution of the process gases has been shown to lead to a more stable material which has microcrystalline inclusions and a low density of microvoids [22]. Recently, similar two-phase materials have been prepared by PECVD using parameters close to the range where powder formation takes place. It was shown that such material has very attractive electronic properties and appears to be more stable [23].

7.6 Amorphous-Silicon Solar Cells

A particularly important field of application was initiated by the first publication about amorphous-silicon solar cells in 1976 [5]. For this application it is most important that the absorption of a-Si:H in the visible spectral region is considerably larger than in c-Si, thus enabling effective absorption of sunlight in a film which is only about 1 μm thick (Fig. 7.2). In the most commonly used superstrate cell, the structure is glass/TCO/ p^+ -SiC_x/i-a-Si:H/ n^+ -a-Si/metal and the light enters through the glass. The substrate cell uses stainless steel (ss) as the substrate, with an inverted layer sequence ss/Ag-ZnO/a-Si(n^+)/a-Si(i)/a-Si(p^+)/metal grid. In both cells the thickness of the active undoped

absorber layer, a-Si:H(i), is about 0.5 μm , such that carrier collection occurs predominantly by drift in the electric field. Single-junction cells have been developed with stable efficiencies in the range of 9–10% in the laboratory for small areas. A major problem of the amorphous-silicon technology has been the degradation of amorphous films and devices under illumination. Considerable progress has been made concerning increased stability of solar cells by proper device engineering. The strategy is to use stacks of two or three pin cells. Such an advanced device structure offers two advantages: (1) In a stack, the thickness of the individual cells is reduced, which improves the stability by enhancing carrier collection through an increase of the internal electric field. (2) By using materials with different bandgaps, a tandem structure can be made which leads to a better use of the solar spectrum. It is important that the degradation of the cells appears to saturate as a function of the exposure time (typically after 100 h illumination with AM1), such that stabilized efficiencies can be guaranteed by the manufacturers. Optimized solar cells typically degrade by about 10% from the as-deposited state. In recent years several companies have started commercial production of a-Si:H PV modules with stabilized efficiencies in the range 6–8% on large-area substrates.

Figure 7.6 shows the structure of a triple-junction solar cell from United Solar System Corporation (USSC), the most successful cell of this type so far (see [22]). In this structure, the top cell, which absorbs the high-energy part of the solar spectrum, uses a-Si:H with a bandgap of 1.8 eV as the intrinsic layer. The i-layer of the middle cell is an a-Si/Ge alloy which contains

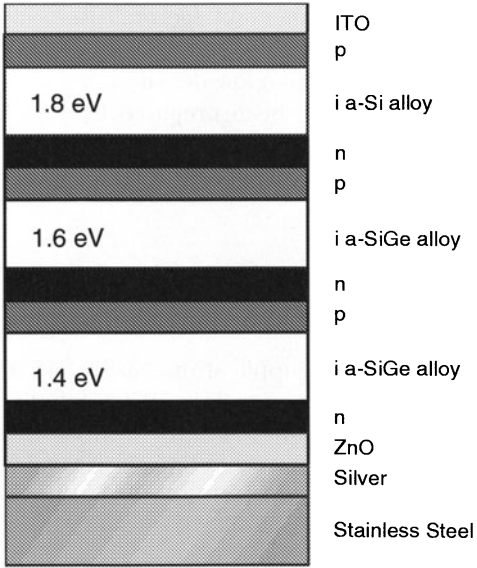


Fig. 7.6. Schematic illustration of a three-junction thin-film solar cell [22]

about 15% Ge, leading to a bandgap of 1.6 eV. The bottom cell, which is designed to absorb the red part of the spectrum, uses an i-layer of an a-Si/Ge alloy with 40–50% Ge and a bandgap of 1.4 eV. A textured Ag/ZnO back-reflector is used to enhance light trapping. Such a structure has led to the highest efficiency (active area) reported so far for laboratory cells ($A = 0.25 \text{ cm}^2$): 15.2% initial, 13% stabilized [22]. The use of high hydrogen dilution in the preparation of the intrinsic films appears to be one of the keys to obtaining these results.

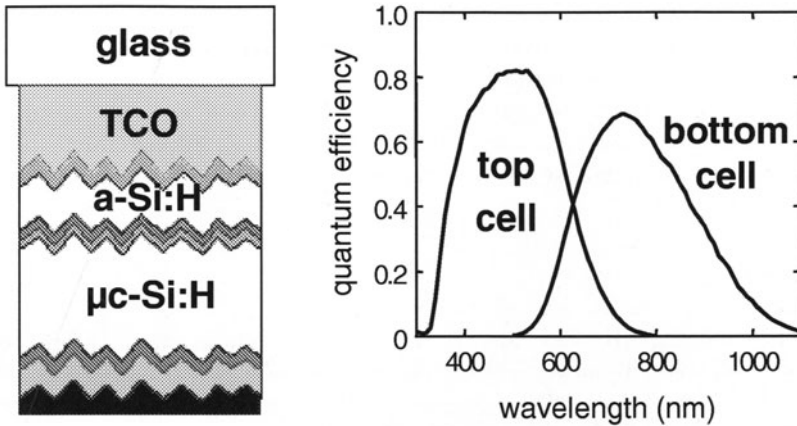


Fig. 7.7. Micromorph solar cell concept: **a** schematic illustration of the cell and **b** quantum efficiencies of the top and bottom cells [26]

The challenges for research at present are the development of materials which can be used in stacked tandem structures with a-Si:H, enhancement of the deposition rate, and improvement of the cell efficiencies and production yields. The a-Si/Ge alloys still have considerably poorer electronic properties than a-Si:H and, in addition, their deposition uses germane as a process gas, which constitutes an important cost factor. Therefore a number of research groups are aiming at replacing the a-Si/Ge alloy with microcrystalline silicon ($\mu\text{c-Si:H}$) [24–26]. $\mu\text{c-Si:H}$ can be prepared by PECVD or HW deposition techniques under conditions which are compatible with those used in the deposition of a-Si:H. The physics of this material is rather complex, owing to pronounced structural heterogeneity. Structural investigations suggest that $\mu\text{c-Si:H}$ consists of small crystallites with sizes in the order of 5–30 nm which are embedded in columns with a diameter of typically 50–200 nm. A strongly disordered phase exists around the columns, which is often referred to as amorphous silicon. It appears that this structure is largely independent of the method used for preparation. These inhomogeneities determine the physical properties and therefore considerably complicate the interpretation of most

experimental results. A comparison of the absorption edges (Fig. 7.2) suggests that one should use this material for a bottom cell in a tandem concept with a-Si:H. Figure 7.7 shows a schematic illustration of such a cell, made up of a stack of two pin structures with a-Si:H forming the top and μ c-Si forming the bottom cell. The resulting quantum yield reveals the advantage of such a device concept: the top cell, made of a-Si:H, uses the high-energy photons, and the bottom cell, made of μ c-Si:H, uses the low-energy photons. Using this promising approach, stabilized efficiencies of about 10% have been demonstrated.

The industrial activity proves impressively that technologies based on a-Si:H and related alloys have surmounted the barrier to commercialization. The progress achieved in this field is certainly based on a broad understanding of the physics of both materials and devices as a result of 25 years of continuous research effort. The numerous applications of these amorphous semiconductors in photovoltaics, sensors, photodetectors and, in particular, displays drove this research and established the mature technology available today.

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