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BY CHEMICAL VAPOR DEPOSITION AND PLASMA HYDROGENATION

THE UNIVERSITY OF ARIZONA  M.S. 1983
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OPTICAL AND ELECTRICAL PROPERTIES OF AMORPHOUS SILICON
PREPARED BY CHEMICAL VAPOR DEPOSITION AND PLASMA HYDROGENATION

by
Gary Louis Scheidegger

A Thesis Submitted to the Faculty of the
COMMITTEE ON OPTICAL SCIENCES (GRADUATE)
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

1983
STATEMENT BY AUTHOR

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H. ANGUS MACLEOD
Professor of Optical Sciences

July 29, 1983
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ABSTRACT

The optical and electrical properties of a-Si films fabricated by chemical vapor deposition are investigated both in the as-deposited form and after post-deposition hydrogenation. Since post-deposited hydrogen has a composition that varies with film depth, three sets of films with differing thicknesses (133, 266, and 532 nm) were prepared at 600 C. Hydrogenation was carried out in a glow discharge at 400 C and 500 C.

Results show order-of-magnitude variations in both dark conductivity and photoconductivity with hydrogenation while the optical constants change very little. Comparisons between samples of different thicknesses result in inconsistencies when the conventional model of hydrogen's effect on a-Si is used. A new model is suggested to explain these inconsistencies.
CHAPTER 1

INTRODUCTION

Much attention has been given in recent years to the use of amorphous silicon (a-Si) as a solar cell material, owing to its low cost relative to the crystalline form. The structural defects contained in pure a-Si, however, make it unsuitable for such use. Doping with hydrogen is found to greatly reduce the effect of these defects, making it a promising photovoltaic candidate. In this chapter, the requirements of a good photovoltaic material are considered, followed by a discussion of the properties of both crystalline and amorphous silicon. A summary of a-Si fabrication methods is then presented.

The Photovoltaic Effect

The photovoltaic effect, which converts absorbed radiation directly into electrical energy, was first reported in solid state systems by Adams and Day (1876). It results from basic thermodynamic principles, which will be described for the common case of the p-n junction. Other types of junctions follow similar principles.

When a junction is formed between a p-doped semiconductor and an n-doped semiconductor, the electrons and holes will diffuse across the junction, leaving a net positive charge on the n side and a net negative charge on the p side. The electric field thus formed then
acts as a barrier to further diffusion. The equilibrium charge distribution is reached when the electrons and holes have minimized their Gibbs free energy, balancing their affinity for lower energy and greater entropy.

If an incident photon has sufficient energy, it can excite an electron from the valence band to the conduction band, creating both a free electron and a free hole. These will wander about randomly until they either recombine or encounter the electric field at the junction. In the former event, nothing is gained. In the latter event, however, they will be driven by the field, thus becoming available for work in an external circuit.

**Material Properties of Interest**

The above analysis immediately suggests two material properties that influence the efficiency of the solar cell. The first is the probability that a photon having sufficient energy will excite an electron-hole pair. Since this is likely to be the primary absorption mechanism for photons of energy greater than the bandgap, we usually discuss this property in terms of the absorptance of the material. The second is the probability that a hole or electron will encounter the electric field at the junction. We usually relate this property to the diffusion length of the hole or electron (how far it is likely to wander without recombination), the extent of the junction, and the thickness of the cell. Although the diffusion length is difficult to measure, various easily measured electrical properties can be related to it as explained in Chapter 2. The active thickness of the cell
(d_{\text{act}}) is determined by the absorption coefficient ($\alpha$) for solar radiation at photon energies greater than the bandgap, together with the diffusion length ($l_{\text{diff}}$). At a depth of $1/\alpha$, most of the incident light has been absorbed, so $d_{\text{act}} \leq 1/\alpha$. However, carriers generated far from the junction cannot reach it, so $d_{\text{act}} \leq l_{\text{diff}}$. For maximum utilization of the incident light, most of the light should be absorbed within the active thickness. We should therefore have $l_{\text{diff}} \geq 1/\alpha$.

A less obvious material property of concern to efficiency is the size of the bandgap, $E_g$. If a photon with energy less than the bandgap is incident, it will not excite a charge carrier pair and its energy will be lost. On the other hand, the probability of an energetic photon exciting more than one pair is very small. Typically, an energetic photon will excite an electron to a level high in the conduction band. Then, through phonon interactions, the electron falls to the bottom of the conduction band, losing its extra energy as heat. If we assume that the maximum work available from a photon of energy $h\nu$ is $E_g$ if $h\nu \geq E_g$ and 0 if $h\nu < E_g$, then for any given photon source and material bandgap there is a maximum theoretical efficiency assuming all other losses are zero. This concept is illustrated in Figure 1.1, which shows the solar photon flux vs. $h\nu$ for the sun directly overhead on a clear day at sea level (called air mass one or AM1 illumination). The number of usable photons incident per square meter of solar cell per unit time may be found from Figure 1.1 by integrating from $h\nu = E_g$ to infinity. The maximum power output is then found by multiplying this result by $E_g$, the usable energy in each photon. The maximum possible efficiency of the solar cell is obtained by dividing by the
Figure 1.1. AM1 Spectral Photon Flux as a Function of Photon Energy.

The shaded area indicates the usable photons for a photovoltaic device made from a-Si. After Thekaekara (1974).
total AM1 power density, 960 W/m$^2$ (Thekaekara, 1974). Figure 1.2a shows this maximum efficiency as a function of bandgap. Further assumptions about the nature of p-n junctions and carrier mobility, as discussed in Backus (1980), reduce the maximum expected efficiency as shown in Figure 1.2b. Also shown in Figure 1.2b are the bandgaps of various semiconductor materials with their corresponding maximum efficiencies.

Ultimately, the economics of the solar cell will determine whether it is to be widely used as an energy source. A central concept in solar cell economics is the energy payback time, the period the cell must be operated to generate the energy used in its manufacture. The importance of the energy payback time lies in its rating of an energy production system independently of the prevailing cost of energy. It should be a small fraction (<10%) of the lifetime of the cell.

The actual cost of the solar cells is important as long as there are competing energy sources. Hovel (1980) expects that a competitive solar cell for residential power generation must cost no more than $.70/W_p, where W_p denotes peak watt or the power output at peak power generation. The use of photovoltaics in central power plants will require even lower costs ($.15 to $.40/W_p) because of the need for storage, reliability, investor dividends, etc.
Figure 1.2. Maximum Theoretical Efficiency as a Function of Bandgap Under AM1 Illumination.

a. Assuming only that the work available from a photon is $E_g$ if $hv \geq E_g$ and 0 if $hv < E_g$. After Wolf (1981), p. 24-27.

Crystalline Silicon

Single crystal silicon (c-Si) is the most common solar cell material in use today, not because of economics but because by straightforward though costly procedures it has been developed into a reliable technology. Its principal advantage is its long carrier diffusion length (85 μm, Kumari, Arora, and Jain, 1981). Efficiencies of up to 20% have been reported for c-Si solar cells under concentrated sunlight (Hersch and Zweibel, 1982). The manufacture of single crystal silicon, however, is a long and energy intensive process. Currently, such cells have an energy payback time of several years.

To manufacture crystalline silicon, naturally occurring silica (SiO₂) must first be reduced and purified. This raw material must then be processed to form the single crystal solar cell (see Hersch and Zweibel, 1982, for details). The processing procedure has been steadily refined over the past 30 years, while the cost of producing the raw material has not changed significantly. Even if the processing were free, c-Si solar cells would cost $3/Wp, which is too much to be competitive with conventional sources (Seraphin, 1982).

If the cost of the raw material cannot be reduced, we must make the cell as thin as possible so as to use less of it. For c-Si, 1/α is approximately 3 μm at hν = 2 eV (see Figure 2.1, page 18). The optimum thickness for a c-Si solar cell is thus about 3 μm, which is the domain of thin film technology. However, single crystal silicon cannot be produced by thin film techniques without the use of a single crystal substrate; currently, the thinnest realizable cell not seeded from a single crystal substrate is about 500 μm.
Amorphous and polycrystalline silicon can be deposited as thin films. The cost of manufacture of these forms is thus anticipated to be much less than for crystalline silicon. Both of these forms, however, have reduced diffusion lengths owing to carrier trapping and recombination at dangling bond sites (in the case of amorphous silicon) or grain boundaries (in the case of polycrystalline silicon). Solar cells fabricated from polycrystalline silicon have achieved 13% efficiency (Kumari et al., 1981), while the maximum reported efficiency for a-Si solar cells is 9.2% (Hamakawa, 1982).

**Amorphous Silicon**

An ideal amorphous structure is one in which each atom retains its crystalline coordination, tetrahedral in the case of silicon, but with small variations in bond lengths and angles that eliminate the long-range order (Tsu, 1981). In the case of a-Si, however, the coordination number is too large to accommodate an ideal amorphous structure. Certain structural defects such as dangling bonds, strained bonds, and microvoids must be tolerated (Kaplan, 1979a).

Dangling bonds are thought to be the most important structural defects in chemical vapor deposited a-Si since the high deposition temperatures employed result in a highly coordinated material of 97% to 98% crystalline density (Wohlgemuth et al., 1982). Instead of bonding to four other Si atoms, some atoms find only three, leaving one of their bonding electrons "dangling". The energy of this electron state falls inside the bandgap of the material, and its spatial occupation density is localized. Since the electrons in these dangling bonds are
unpaired, their density can be measured by electron spin resonance (ESR). Dangling bonds inhibit solar cell performance since they act as nonradiative electron-hole recombination centers and carrier traps (Street, Knights, and Biegelsen, 1978). Hence, the carrier diffusion length is greatly reduced.

Central to an understanding of the electrical and optical properties of a-Si are the nature and density of its electron states. Like c-Si, a-Si has states whose spatial occupation density is uniform throughout the material with variation only on the atomic scale. These are called extended states and are organized into bands as in other semiconductors. In particular, a-Si has a valence band and a conduction band with the Fermi level in between. The energy difference between the highest valence band state and the lowest conduction band state is called the "extended state bandgap".

Moreover, we find in a-Si localized states with energy levels inside the extended state bandgap. Different models for the density of these states as a function of energy have been proposed. The one that agrees best with experimental results is that proposed by Mott, Davis, and Street (1975) as shown in Figure 1.3a. There is, at present, no reliable method for measuring the bulk density of states as a function of energy level in a-Si. Figure 1.3b shows the density of states obtained by Fujita and coworkers (1981) by the field effect technique for chemical vapor deposited a-Si deposited at 600 °C. Values obtained by the field effect technique, however, are greatly influenced by the surface density of states, which is larger than the bulk (Lachter, Weisfield, and Paul, 1982). Furthermore, the existence of the local
Figure 1.3. Density of States as a Function of Energy Level.

a. Density of states model for amorphous silicon or germanium; after Mott and coworkers (1975). $E_X$ are acceptors and $E_Y$ are donors due to the same defect centers.

b. Experimental density of states for chemical vapor deposited a-Si (deposition temperature = 600 C) by the field effect technique; after Fujita and coworkers (1981).
maxima at $E_x$ and $E_y$ has been the subject of some controversy (Fritzsche, 1980). Regardless of the existence of actual maxima, the symbols $E_x$ and $E_y$ are used to denote corresponding general areas on the density of states curve.

The localized states near the extended state bands (between $E_V$ and $E_B$ and between $E_A$ and $E_C$ in Figure 1.3) are called band tails and are due to the lack of long-range order in the amorphous lattice. They would exist even if the lattice were ideal. The other gap states are generally ascribed to lattice defects (such as dangling bonds), and their density varies with the method of preparation (Mott et al., 1975; Nandan, Le Comber, and Spear, 1976). The energies of states associated with different defects of the same type vary owing to different local environments, so a continuous density of states is observed.

In addition to reducing the free carrier diffusion length, gap states in the undoped material tend to prevent doping from being effective. This occurs when the number of gap states intentionally added by doping is small compared to the number already present in the undoped material. Since the density of states distribution is not changed significantly by the dopant atoms, the Fermi level does not move toward the band edge. Hence, no p- or n-type behavior will be observed.

A thorough discussion of the relationship between defects, spins, and states may be found in Vogel-Grote and coworkers (1980).
Deposition Methods of Amorphous Silicon

Physical Vapor Deposition

Physical vapor deposition (PVD) removes silicon atoms from a source material and transports them to a substrate where they condense to form the thin amorphous film. To permit condensation, the substrate must be cooler than the incident atoms. The lack of thermal equilibrium between the impinging atoms and the substrate causes internal stress and less than ideal bonding.

There are two primary techniques for removing atoms from the source material. In the evaporation technique, the source is heated to boil off atoms. This is accomplished with either an electron beam or resistance heating. Pressures on the order of $10^{-8}$ torr are required to prevent contamination (Thomas et al., 1978). Doping is accomplished by either coevaporating the dopant material or including a gaseous compound of the dopant material in the chamber. Sputtering, on the other hand, uses a glow discharge to generate ions (usually argon), which then bombard the source material. The argon pressure must be low (0.001 to 0.1 torr) both to allow the glow discharge (see below) and to reduce Ar incorporation in the film. Doping is accomplished by including a gaseous compound of the dopant material in the chamber. Sputtering has the additional disadvantage that the atoms arrive at the substrate with high velocity and can structurally damage the already deposited film before becoming incorporated. Both PVD methods, however, result in silicon films with similar properties (Theye, 1976).
Glow Discharge

In the glow discharge (GD) process, a gaseous silicon compound, usually silane (SiH₄), flows over the substrate while being broken apart by free electrons accelerated by an electric field. The gas itself is the source of electrons since electron-molecule collisions produce more free electrons in addition to breaking the molecules apart. The electric field may be oscillating (usually at radio frequencies, rf) or constant (dc). An rf field may be produced either inductively or capacitively, whereas dc fields can only be produced capacitively.

At atmospheric pressure, the mean free path of electrons in the gas is too short for them to build up sufficient energy to break the gas molecules apart. Pressures on the order of 0.1 to 1 torr must be used for the glow discharge to be effective.

Doping is achieved by mixing the silane with a gaseous compound of the desired dopant.

Chemical Vapor Deposition

Like GD, chemical vapor deposition (CVD) uses silane gas as the source material. However, CVD uses higher deposition temperatures (550 to 650 C) to break up the silane thermally, thus eliminating the need for the glow discharge. Also, since no glow discharge is required, it is possible to use CVD at atmospheric pressure. This opens the way for large flow-through production, which would be more efficient and economical than vacuum systems.
The Solar Energy Group at the Optical Sciences Center of the University of Arizona has used CVD for the deposition of a-Si for photothermal solar energy conversion (see, for example, Seraphin, 1976; Booth, 1980). More recently, the group has been studying CVD a-Si with the objective of improving its suitability for photovoltaic applications (Raouf, 1981; Hey, 1981; Hey et al., 1981; Schay, 1981; Strobl, 1981; Köberle, 1982; Hey and Seraphin 1982). CVD was used to deposit all samples used in this study.

The Role of Hydrogen in Amorphous Silicon

Among the various methods of manufacturing amorphous silicon, only CVD grows the film in thermal equilibrium with the substrate. This results in a film thought to be free of most defects except dangling bonds. Owing to a deposition temperature much lower than that used in CVD, material deposited in a glow discharge contains significant amounts of hydrogen that neutralize these dangling bonds (as explained in Chapter 2), thus avoiding trapping of the carriers. Deposited at 550°C or above, CVD material is practically void of hydrogen, and dangling bonds are abundant. This handicap can be removed by diffusing hydrogen into the material after deposition. This not only makes material fabricated by CVD competitive with that prepared by GD, but may even result in films of superior photoelectric properties owing to the absence of other defects.

Post-deposition hydrogenation has the drawback that the hydrogen must be diffused into the material. This results in an inhomogeneous hydrogen concentration profile, with hydrogen content
decreasing from the front surface to the back surface. In this thesis, the effects of this inhomogeneity on the optical and electrical properties of the material are studied. Results show that for hydrogenation at 500 C the diffusion depth is sufficient to reduce hopping conductivity greatly. However, even the front surfaces of the films are not saturated\(^1\) with hydrogen with respect to photoresponse at this temperature, resulting in less than maximum photoconductivity. It was determined that the results of this study cannot be explained with the present understanding of the effect of hydrogen as outlined in Chapters 1 through 3. We therefore propose a new model, which attributes most of the photoconductivity effect to interstitial hydrogen while attributing dark conductivity and bandgap effects to bonded hydrogen.

\(^1\) See Glossary.
CHAPTER 2

THE INFLUENCE OF STRUCTURE AND COMPOSITION
ON THE PROPERTIES OF AMORPHOUS SILICON

Since the thickness of the solar cell and its means of fabrication determine overall costs, thin films promise to make large-scale photovoltaic energy conversion economically attractive. Unfortunately, all Si thin film deposition methods result in either amorphous or polycrystalline films. In polycrystalline films, the grain boundaries serve as electron-hole recombination sites and electrical shorts, reducing the diffusion length and making the film unsuitable for photovoltaic applications. In amorphous films the same problems are encountered owing to dangling bonds, strained bonds, and microvoids.

The challenge to amorphous thin film technology is to minimize the effects of these defects either by reducing their number through variation of the deposition parameters or post-deposition annealing, or by passivating them with dopants such as hydrogen. The most effective deposition parameter at our disposal is the deposition temperature; the greater the deposition temperature, the more closely the Si atoms orient themselves to the ideal tetrahedral coordination with minimum strain. The same temperature effect is present during post-deposition anneal; the spin density (from ESR measurements) of pure amorphous silicon deposited at room temperature and annealed at T is similar to that deposited at T (Thomas et al., 1978).
Another approach is doping with hydrogen, which can terminate the dangling bond of a triply-coordinated Si atom. In so doing, bonding and antibonding states are formed that have energy outside the bandgap or, at worst, just inside the bandgap (Moustakas, Anderson, and Paul, 1977). At the same time, two electrons are paired in the Si-H bonding state, eliminating the ESR produced by a lone electron in a dangling bond.

The bonding and antibonding states of a strained or weak Si-Si bond may also have energies inside the bandgap (Madan et al., 1976). Hydrogen may break such bonds and attach itself to the resulting dangling bonds, thereby relieving the strain and driving these states out of the gap as well (Knights, 1980). In this case, however, no reduction in the ESR signal will be observed since two electrons were paired originally in the Si-Si bonding state.

In this chapter, the optical and electrical properties of a-Si are discussed, with emphasis on the role of localized gap states and incorporated hydrogen. The various methods of a-Si fabrication are then discussed, with emphasis on the effect of the preparation parameters on the spin density of the resulting material. Chemical vapor deposited a-Si will be treated in Chapter 3.

Optical Properties

Amorphous silicon has a much higher absorption coefficient than the crystalline form, which may compensate for its shorter carrier diffusion length by allowing the photogenerated carriers to be created nearer the junction. Referring to Figure 2.1, the absorption
Figure 2.1. (ahv)$^{1/2}$ vs. hv for c-Si and a-Si by Various Deposition Methods and Temperatures.

Curve 1: dc glow discharge, substrate at anode, $T_D = 25$ C
Curve 2: dc glow discharge, substrate at cathode, $T_D = 270$ C
Curve 3: dc glow discharge, substrate at anode, $T_D = 270$ C
Curve 4: dc glow discharge, substrate at cathode, $T_D = 25$ C
Curve 5: sputtered, $T_D = 25$ C
Curve 6: sputtered, $T_D = 25$ C, annealed at 400 C for 2 hours
Curve 7: chemical vapor deposited, $T_D = 600$ C

Curves 1 through 6 and c-Si after Fritzsche, Tai, and Persans (1978); curve 7 after Janai and coworkers (1979).
coefficient of a-Si for $h\nu = 2$ eV is between $9 \times 10^3$ and $2 \times 10^5$ cm$^{-1}$, depending on the method of preparation. For c-Si, it is $3.6 \times 10^3$ cm$^{-1}$.

The higher absorption coefficient of amorphous silicon is due to a relaxed requirement for momentum conservation. Since c-Si is an indirect gap semiconductor, its band structure prevents conservation of both energy and momentum in a simple photon-electron interaction where the photon energy is near the bandgap. In c-Si, a phonon must participate in the interaction for such a photon to be absorbed. In a-Si, the lattice as a whole may enter into the balance from the beginning, making a phonon unnecessary. Grigorvici and Vancu (1968) explain such interactions as a direct consequence of the disorder of the lattice. They propose that "the local deformation of the lattice by thermal motion and not the lattice vibration itself is responsible for the conservation of momentum" in crystalline silicon (authors' emphasis).

As seen in Figure 2.1, a plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for amorphous silicon is found to be linear for $\alpha > 3 \times 10^4$ cm$^{-1}$. The linear portion of the curve presumably involves only extended-state transitions. The nonlinear portion (or absorption tail) is ascribed to photo-excitations involving localized states (Theye, 1976), although tails for $\alpha < 10^3$ cm$^{-1}$ may also be ascribed to measurement errors such as light scattering (Fritzsche, 1980). The intercept of this graph with the $h\nu$ axis should therefore give a good indication of the extended state bandgap (Theye, 1976). This intercept is called the "optical bandgap" and is denoted $E_0$. 
Based on the theory of Grigovici and Vancu, Tsu (1981) claims there is a direct correlation between the slope of \((a\nu)^{1/2}\) vs. \(\nu\) and the amorphousness of the silicon lattice.

A reduction in the absorption coefficient (that is, a shift of the absorption edge to higher photon energies) in both the linear and nonlinear portions of the curve can be achieved either by annealing pure a-Si (see Figure 2.1) or by hydrogenation (Fritzsche, 1980). The index of refraction \((n)\) is also reduced by anneal (Brodsky et al., 1970) and hydrogenation (Black, 1980). Both of these processes reduce the spin density and the density of localized states in the gap.\(^1\) The reduction in \(n\) has been explained as a reduction in effective polarizability as the spin density is reduced (Schwidefsky, 1973). A reduction in localized gap states has been credited with reducing \(\alpha\) as well, even for \(\alpha > 3 \times 10^4\) cm\(^{-1}\) (Kaplan, 1979b). Others have related the absorption edge shift to the total amount of hydrogen in the material, noting that Si-H has a larger binding energy than Si-Si (Fritzsche, 1980). Since \(n\) and \(\alpha\) are related by the Kramers-Kronig relations, whatever explanation is offered for one must also apply to the other.

**Electrical Conduction**

Conduction in a-Si is carried out by charge carriers (electrons and holes) in both the extended and localized states. The mobility of

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1. Both annealing and hydrogenation reduce the spin density when acting alone. However, annealing a film that already has incorporated hydrogen causes the hydrogen to evolve so that the net effect on spin density will depend on the balance between the two processes (see Figure 2.2, page 25).
carriers in the extended states is much greater than of those in localized states; the extended state bandgap is sometimes called the "mobility gap". Localized state conduction is carried out by carrier tunneling (hopping) from state to state and is usually called "hopping conduction". One or the other type of conduction will usually dominate depending on the relative numbers of carriers in each type of state and their mobilities.

In a semiconductor, temperature determines the conduction mechanism predominantly through its effect on carrier populations. At low temperatures, the electrons occupy almost all of the states below the Fermi level and leave almost all the states above it unoccupied. Hence, there are very few free electrons in the conduction band or free holes in the valence band of the undoped material. However, since there are localized states in close proximity (on the energy scale) both above and below the Fermi level (see Figure 1.3), electrons may be excited from localized states below the Fermi level to localized states above it, creating localized electron-hole pairs. At high temperatures, electrons may be more highly excited than at low temperatures. As the temperature rises, more and more free carriers are generated until their contribution to the overall conductivity is greater than that of the localized carriers.

Free carriers may be thermally excited in one of three principal ways: First, an electron may be excited from $E_g$ to $E_C$, creating both a free electron and a free hole. Second, an electron
may be excited from $E_Y$ to $E_C$ (see Figure 1.3),\(^1\) creating a free electron and a localized hole. Finally, an electron may be excited from $E_Y$ to $E_X$, creating a free hole and a localized electron. Although free and localized carriers are being created at the same time, the free carriers will dominate the conductivity at high temperatures owing to their greater mobility.

Complementary to the process of thermal excitation is thermal de-excitation. The localized gap states serve not only as sources of free carriers at high temperature but as efficient carrier traps, trapping even those free carriers that were excited as pairs (the first of the above mechanisms). The free carrier diffusion length is thus reduced when localized gap states are present. At high temperatures, where free carrier pair excitations are significant, the conductivity of samples having a greater density of localized gap states will thus be less than for samples with fewer gap states. At low temperatures, on the other hand, where hopping conduction is dominant, samples having more gap states will have greater conductivity than those with fewer gap states.

In the presence of illumination, free carriers may be generated by photon absorption. If this process dominates thermal excitation, free carrier conduction will dominate at all sample temperatures. Carrier trapping will thus reduce the photoconductivity (conductivity

\(^1\) In this discussion, the energies $E_V$, $E_Y$, $E_X$, and $E_C$ are used to denote general regions on the energy spectrum, not exact energies. Hence, $E_Y$ refers generally to the valence band, while $E_Y$ refers to localized states between $E_Y$ and $E_F$. 
in the presence of illumination) of samples having a greater density of localized gap states below those with fewer gap states regardless of temperature.

Dark and photoconductivity curves illustrating the phenomena discussed above are presented in Chapter 3.

**Pure Amorphous Silicon**

Pure amorphous silicon can be produced only by PVD since both the GD and CVD material have incorporated hydrogen. The defect density in the pure material can be adjusted only through the deposition parameters, temperature and pressure being the most important, or by post-deposition annealing.

If the pressure is low enough to avoid contamination, only the temperature of deposition \( (T_D) \) has a significant effect on the spin density \( (N_S) \) of the material deposited (Thomas et al., 1978). At greater deposition temperatures, the atoms have greater mobility within the growing film and are more likely to find their ideal coordination. Included in Figure 2.2 (page 25) is \( N_S \) as a function of \( T_D \) for pure amorphous silicon evaporated at \(<3 \times 10^{-8} \) torr. The lowest spin density obtainable for as-deposited pure a-Si is about \( 3 \times 10^{19} \) cm\(^{-3}\). This can be halved by annealing since it is found experimentally that the films may be annealed up to 560 C without crystallization although they can be deposited only up to 430 C (Thomas et al.).

**Codeposited Hydrogen in Amorphous Silicon**

Amorphous silicon is codeposited with hydrogen when the GD or CVD methods are used, owing to the presence of hydrogen in the silane
molecule. Hydrogen gas can also be introduced into PVD systems and codeposited with the silicon. Figure 2.2 shows $N_s$ as a function of $T_D$ for GD and CVD as well as for pure a-Si. The broad minimum observed around 300 C results from the optimization of two competing growth processes in the GD films. As $T_D$ rises, the films become more ideally coordinated. At the same time, increasing temperature causes more hydrogen to evolve, leaving more uncompensated dangling bonds (Fritzsche et al., 1978).

In addition, it has been suggested that the hydrogen in the silane molecule increases the surface mobility of adsorbed atoms during deposition, allowing them greater freedom to find ideally coordinated sites (Knights, 1980). Evidence can be seen in $N_s$ vs. annealing temperature curves for samples deposited at room temperature. Such curves have the same form as those in Figure 2.2 but are shifted to higher spin densities (Fritzsche, 1980). We also cannot discount the possibility that the rf electromagnetic field, present during deposition but not during anneal, either contributes to surface mobility or heals defects in the lattice. It should be noted that CVD samples (for which the field is not present during deposition) deposited at temperature $T$ have spin densities comparable to GD samples deposited at room temperature and annealed at $T$.

Anderson, Moustakas, and Paul (1977) reported on the electrical conductivity of a series of samples sputtered with and without

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1. Spin density data also exist for anneal in excess of 450 C. Spin density continues to rise as the anneal temperature increases, clearly identifying a minimum around 300 C.
Figure 2.2. Spin Density as a Function of Deposition Temperature for As-Deposited a-Si by Different Fabrication Methods.

- PVD (sputtered); after Thomas and coworkers (1978)
- CVD; after Hey and Seraphin (1982)
- GD, inductive
- GD, capacitive, substrate at anode
- GD, capacitive, substrate at cathode
  GD after Fritzschke and coworkers (1978)
hydrogen. For a sample sputtered at 250°C in the absence of hydrogen, the conductivity at 40°C was $2 \times 10^{-3} \text{ (} \Omega \text{ cm})^{-1}$. With 8.9 millitorr of H$_2$ in the sputtering gas, the conductivity at 40°C dropped seven orders of magnitude to $3 \times 10^{-10} \text{ (} \Omega \text{ cm})^{-1}$, which is comparable to GD samples deposited at similar temperatures (Chittick, Alexander, and Sterling, 1969; Le Comber, Madan, and Spear, 1972). Pawlik and Paul (1977) reported that 1.8 millitorr of hydrogen in the sputtering gas ($T_D = 250°C$) reduced the spin density of the resulting material to approximately $4 \times 10^{16} \text{ cm}^{-3}$.

Paul and coworkers (1976) reported the first successful doping of sputtered a-Si by adding 0.5 to 0.7 millitorr of H$_2$ along with the dopant (B$_2$H$_6$ or PH$_3$) to the sputtering gas.

**Post-Deposition Hydrogenation of Pure Amorphous Silicon**

The first post-deposition hydrogenation was performed by Le Comber and coworkers (1973), in which they subjected evaporated a-Si to atomic hydrogen produced from H$_2$ by rf glow discharge. They found a decrease in spin density to below their detection limit of $5 \times 10^{17} \text{ cm}^{-3}$. The hopping conductivity of their samples decreased much less than would be expected, however.

In 1978, Kaplan and coworkers reported on the post-deposition hydrogenation of a-Si samples using both molecular and atomic hydrogen. The samples were evaporated under ultrahigh vacuum ($<10^{-8}$ torr) conditions at elevated temperatures ($T_D > 350°C$). They observed no significant effect with the molecular hydrogen, but reported a spin density decrease to below their detection limit of $10^{17} \text{ cm}^{-3}$ with the
atomic hydrogen. Furthermore, they observed a decrease in room temperature dark conductivity to $10^{-7} \ (\Omega \ cm)^{-1}$. The photoconductivity and photoluminescence of the resulting films were comparable to a GD sample deposited at about the same temperature (380 C). However, the amount of hydrogen contained in the PVD sample (3.5 at.%) was less than the comparable GD sample (14 at.%).
CHAPTER 3

CHEMICAL VAPOR DEPOSITED AMORPHOUS SILICON

In codepositing hydrogen with silicon by any method, the improvement in structural order with increasing deposition temperature must be balanced against the evolution of hydrogen. We may attempt to overcome this by depositing the film at high temperatures and then hydrogenating it at lower temperatures. Unfortunately, hydrogen that evolves more slowly (at lower temperatures) is also absorbed more slowly. By separating the process into two steps, however, we are free to extend the hydrogenation time.

Chemical vapor deposition provides us with the highest deposition temperature possible without crystallization (550 C to 650 C) in addition to thermal equilibrium with the substrate; this results in films of 97% crystalline density (Janai et al., 1979) and improved structural order over GD deposited films (Hey and Seraphin, 1982). For these reasons, the Solar Energy Group at the Optical Sciences Center has focused its photovoltaic research on CVD a-Si and its subsequent hydrogenation (Raouf, 1981; Hey, 1981; Hey et al., 1981; Schay, 1981; Strobl, 1981; Köberle, 1982; Hey and Seraphin, 1982).
As-Deposited CVD a-Si

Figure 3.1 shows the variation of dark conductivity with deposition temperature for as-deposited CVD a-Si produced at the Optical Sciences Center. As $T_D$ increases, the dark conductivity for low measurement temperatures increases, consistent with the increasing spin density shown in Figure 2.2. This behavior is due to a reduction in incorporated hydrogen at the higher deposition temperatures as discussed above and shown in Figure 3.2.

The optical constants of CVD a-Si have not been observed to vary with either deposition or anneal parameters, short of crystallization (Janai et al., 1979).

Post-Deposition Hydrogenated CVD a-Si

The post-deposition hydrogenation of CVD ($T_D = 600 \text{ C}$) films was first reported by Sol and coworkers (1980) using both dc and rf generated deuterium plasmas at 400 C. The dc plasma showed fewer etching problems and a more stable glow than the rf.

Experiments with the dc plasma were done first with the plasma turned off during cooldown (plasma off). The resulting deuterium concentration was well fitted to a complementary error function (erfc), with a higher deuterium concentration only in the first few angstroms of the film surface. A second sample was cooled with the glow discharge left on during cooldown (plasma on). This time, deuterium concentrations between 1 and 10 at.% were found as deep as 50 nm
Figure 3.1. Dark Conductivity as a Function of Measurement Temperature ($T_M$) for As-Deposited CVD a-Si of Various Deposition Temperatures.

Sample thickness = 1 μm.
Figure 3.2. Hydrogen Concentration as a Function of Deposition Temperature for As-Deposited CVD a-Si.

into the film. At greater depths, an erfc profile was observed as before with a diffusion constant of $5.8 \times 10^{-14}$ cm$^2$/sec (see Figure 3.3).\(^1\) Experiments with the rf plasma resulted in higher overall deuterium concentrations. The authors suggested that a more intense plasma removes existing surface layers, which act as a barrier to diffusion.

Based on a spin elimination model in which all spins above a critical hydrogen concentration are eliminated and all below that concentration are retained, they report the critical concentration of hydrogen to be $10^{19}$ cm$^{-3}$. This is just the density of spins present in the original material.

The same group later reported on hydrogenations performed at 450 C and 500 C (Dieumegard, Dubreuil, and Proust, 1979). The 450 C hydrogenation was performed in an rf plasma and the 500 C hydrogenation was dc. All samples were deposited at 600 C. The results were qualitatively the same as for the 400 C hydrogenations. At 500 C, however, the surface hydrogen layer (the part not fitting the erfc profile) for plasma-on conditions extended 200 nm into the film. All other factors being equal, the surface concentration at 400 C was twice that at 500 C for both plasma on and plasma off, but the

\(^1\) By Fick's second law (Crank, 1956, p. 19), the diffusion of a substance A into a material B will result in a concentration profile proportional to $\text{erfc}[x(4Dt)^{-1/2}]$, where $x$ is depth into B, $t$ is time of diffusion, and $D$ is the diffusion constant. Since $D$ decreases with temperature, the concentration profile that results when the glow discharge is left on during cooldown will not conform to a complementary error function of any unique $D$. However, good fits are found at sufficient depth into the film, while the front surface holds a larger concentration of hydrogen than would be predicted by extrapolating the deep profile.
Figure 3.3. Deuterium Concentration Profiles for CVD a-Si (T_D = 600 C) Deuterated at 400 C.

(a) dc plasma, plasma off during cooldown
(b) dc plasma, plasma on during cooldown
(c) rf plasma, plasma off during cooldown

After Sol and coworkers (1980).
diffusion constant for the 500 C hydrogenation was $2.5 \times 10^{-12}$ cm$^2$/sec.

The hydrogen concentration profiles for the hydrogenation at 450 C and 500 C are shown in Figure 3.4.

Conductivity Effects

Previous CVD a-Si investigations at the Optical Sciences Center have centered around the measurement of its electrical properties with varying deposition and hydrogenation parameters. For all work done here, an rf plasma was used and left on during cooldown down to 200 C.

Schay (1981) reported on the variation in dark and photoconductivity with hydrogenation time and rf intensity (see Figures 3.5 through 3.8) for samples deposited at 600 C. The patterns show improved electrical properties$^1$ as each of these parameters is increased.$^2$ Schay's results are explained if we assume that increasing each of the two hydrogenation parameters results in a greater quantity of incorporated hydrogen.

Hey and Seraphin (1982) reported on the variation in dark and photoconductivity for samples deposited at various temperatures

---

1. "Improved electrical properties" are greater dark conductivity at high measurement temperatures (>60 C), lower dark conductivity at low measurement temperatures (<-40 C), and greater photoconductivity at all measurement temperatures. These result from a reduction of localized states in the bandgap, resulting in greater carrier mobility (diffusion length). The lower dark conductivities for low measurement temperatures are the result of decreased hopping conduction. (See Chapter 2, "Electrical Conduction").

2. Both the largest rf intensity and the longest time of hydrogenation deviate from this pattern. Schay interprets this as an effect of rf etching.
Figure 3.4. Deuterium Concentration Profiles for CVD a-Si ($T_D = 600$ C) Deuterated at 450 C and 500 C.

a. Deuterated at 450 C for 1 min in an rf plasma, plasma off during cooldown.

b. Deuterated at 500 C for 5 min in a dc plasma.

After Dieumegard and coworkers (1979).
Figure 3.5. Dark Conductivity of Hydrogenated CVD a-Si vs. Measurement Temperature for Different Rf Intensities During Hydrogenation.

Preparation parameters:
- Deposition temperature: 600 C
- Film thickness: 400 nm
- Hydrogenation temperature: 400 C
- Hydrogenation time: 30 min

An rf intensity of 27.5 corresponds to an rms electric field strength at the inductive coil of 0.66 V/cm (see Chapter 5).

Figure 3.6. Photoconductivity of Hydrogenated CVD a-Si vs. Measurement Temperature for Different Rf Intensities During Hydrogenation.

Preparation parameters:
- Deposition temperature: 600 C
- Film thickness: 400 nm
- Hydrogenation temperature: 400 C
- Hydrogenation time: 30 min

Figure 3.7. Dark Conductivity of Hydrogenated CVD a-Si vs. Measurement Temperature for Different Times of Exposure to the Hydrogen Glow Discharge.

Preparation parameters:
- Deposition temperature 600 C
- Film thickness 260 nm
- Rf intensity 27.5
- Hydrogenation temperature 400 C

Hydrogenation times (min) are given in the figure.

Figure 3.8. Photoconductivity of Hydrogenated CVD a-Si vs. Measurement Temperature for Different Times of Exposure to the Hydrogen Glow Discharge.

Preparation parameters:
Deposition temperature 600 C
Film thickness 260 nm
Rf intensity 27.5
Hydrogenation temperature 400 C

Hydrogenation times (min) are given in the figure.

(550 C to 650 C) and subsequently hydrogenated under the same conditions ($T_H = 400$ C, other parameters the same as used in this study; see Table 5.4, page 62). Their results are shown as Figure 3.9. Notice that photoconductivity as well as dark conductivity improves with decreasing deposition temperature, indicating that codeposited hydrogen is also contributing to the photoconductivity in the hydrogenated material. We cannot say that there is a linear relationship between hydrogen concentration and photoresponse starting from 0, since little or no photoresponse is observed either for the lowest deposition temperature in the absence of hydrogenation or the highest deposition temperature with hydrogenation. We can imagine several explanations for this. One is that there is a threshold amount of hydrogen below which little change in photoresponse is observed; another is that the rf field somehow activates the hydrogen already present in the as-deposited material. The explanation preferred by Hey and Seraphin, however, is that the hydrogen incorporated during deposition acts as a catalyst for the subsequent hydrogenation.

Optical Effects

The effects of post-deposition hydrogenation on the optical properties of CVD a-Si have not been well studied. The results of one report (Kaplan, 1980) indicate that hydrogen decreases the absorption coefficient ($\alpha$) in the nonlinear portion of the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curve (attributed to localized gap states; see Chapter 2) but leaves the optical bandgap unchanged.
Figure 3.9. Dark Conductivity and Photoconductivity of Hydrogenated CVD a-Si vs. Measurement Temperature for Different Deposition Temperatures.

- Dark conductivity
- Photoconductivity

Hydrogenation temperature = 400 C. After Hey and Seraphin (1982).
CHAPTER 4

EXPERIMENTAL PROCEDURE

We aimed in this study at a determination of the optical and electrical properties of amorphous silicon thin films before and after the insertion of hydrogen into the material. Since the hydrogen was introduced by diffusion through the front surface, the thickness of the film was of critical importance.

These goals determined the basic experimental procedure. We had to deposit films with closely controlled thicknesses. The "before" and "after" condition with respect to hydrogenation required that all other procedures be identical and "nondestructive" in the sense that no variation other than the hydrogenation was introduced in between the two measurements. Consequently, all procedures had to be closely controlled, and strict cleanliness was required to minimize random contamination.

A set of samples varying in thickness around three values (133, 266, and 532 nm) was prepared. The three values were initially set during deposition by observing the sequence of interference fringes in reflection, as described in Chapter 5. A more accurate value was obtained after deposition (for optically measured samples from the two thicker series) by observing transmittance minima in the infrared as described in Chapter 6.
Identity of the "before" and "after" condition could easily be obtained with optical measurements. Neither reflectance nor transmittance measurements required destructive operations such as the attachment of contacts. This is fortunate, since the change of the optical properties between "before" and "after" is predicted to be small, and destructive operations could easily have obscured these small changes. It is for this reason that we determined the optical effects on one set of samples, and the much larger electrical effects on another. It was then possible to perform the optical measurements on the same sample before and after hydrogenation. In principle, the contacts could have been etched from the as-deposited samples for hydrogenation and subsequent optical and electrical measurements. This would have been sufficiently destructive, however, to make the assumption of an identity other than hydrogenation doubtful.

For conductance measurements, we relied on the assumption that samples deposited simultaneously were identical except for hydrogen; "as-deposited" or "before" measurements were performed on a different set of samples than "hydrogenated" or "after" measurements. Furthermore, the thicknesses set by the deposition monitor were taken to be accurate since small variations in thickness matter little to the large conductance effects.

Table 4.1 gives the overall experimental procedure, in chronological order, used to produce the results reported in this thesis. After each step is given the chapter in which a description of that step may be found.
Table 4.1. Overall Experimental Procedure

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Substrate cleaning</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>2.</td>
<td>Sample deposition</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>3.</td>
<td>Back etching</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>4.</td>
<td>Optical measurements of as-deposited samples</td>
<td>Chapter 6</td>
</tr>
<tr>
<td>5.</td>
<td>Electrical contacting of as-deposited samples</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>6.</td>
<td>Conductance measurements of as-deposited samples</td>
<td>Chapter 7</td>
</tr>
<tr>
<td>7.</td>
<td>Hydrogenation</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>8.</td>
<td>Optical measurements of hydrogenated samples</td>
<td>Chapter 6</td>
</tr>
<tr>
<td>9.</td>
<td>Electrical contacting of hydrogenated samples</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>10.</td>
<td>Conductance measurements of hydrogenated samples</td>
<td>Chapter 7</td>
</tr>
</tbody>
</table>
CHAPTER 5

SAMPLE PREPARATION

In this chapter are discussed the instruments and procedures used to prepare samples for measurement. Wherever the evaluation of results had to assume that they were obtained on an identical set of samples, a given step in the preparation of that set was performed simultaneously on all samples in the set.

The Substrates

The substrates used for this study were optically polished sapphire obtained from Wolff Engineering Corporation (Newport Beach, Calif.). Their dimensions were 0.480 x 0.350 x 0.020 in. Sapphire was chosen as the substrate material because of its optical properties and resistance to the chemicals HF and HNO₃ used in the sample preparation as described below.

The substrates were cleaned immediately prior to deposition by soaking them in various solvents and rinses according to Table 5.1. The previous practice of storing batches of cleaned substrates prior to deposition resulted in inconsistent film properties, indicating that some substrate contamination occurred during storage.

Sample Deposition

The CVD reactor system used to deposit the samples is an Applied Materials (Santa Clara, Calif.) AMI-704 Mini-Reactor, originally
Table 5.1. Substrate Cleaning Procedure

<table>
<thead>
<tr>
<th>Solvent or rinse</th>
<th>Time (min)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone and isopropyl alcohol</td>
<td>20</td>
<td>1:1 mixture</td>
</tr>
<tr>
<td>Deionized</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromerge° (H₂CrO₄ + H₂SO₄)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Deionized water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>30</td>
<td>Heated to 80 °C</td>
</tr>
<tr>
<td>Deionized water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deionized water</td>
<td>23</td>
<td>Ultrasonic rinse</td>
</tr>
<tr>
<td>Deionized water</td>
<td>&gt;40</td>
<td>Ultrasonic rinse; substrates remained in rinse until ready for deposition</td>
</tr>
<tr>
<td>Dry nitrogen</td>
<td></td>
<td>Blow dry</td>
</tr>
</tbody>
</table>
designed for the preparation of n-type epitaxial CVD silicon. It was modified by the Solar Energy Group to handle a greater variety of source gases. However, only silane was used in this study. Figure 5.1 schematically shows the entire system.

The silane enters the system through the diffuser block and flows over the substrate, which rests on the graphite susceptor. The susceptor is heated by radiation, while the quartz walls of the reactor vessel are cooled by flowing air. In this manner, the silane decomposes primarily on the susceptor and the substrate, not in the space above the substrate. The unused silane passes through a scrubber and is vented. An extensive technical discussion of the system and its operating procedure is found in Booth (1980). The only deviation from the procedure reported there was that the deposited samples were allowed to cool to near room temperature in a helium atmosphere to minimize the thickness of the surface oxide layer.

The thickness of the growing silicon film was monitored by observing reflection fringes for a wavelength selected by a filter. For films reported in this thesis, light at 997 nm was used. Taking into account the refractive index of a-Si, each interference fringe at this wavelength represents 133 nm of film thickness.

The results of three deposition runs are reported in this thesis. All parameters other than the deposition time were the same for all three runs and are given in Table 5.2. A distinction is made between source and carrier gases only because they came from different tanks and had separate flow meters.
Figure 5.1. Schematic Diagram of the CVD System.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source gas</td>
<td>SiH₄(10 vol.%) + He(90 vol.%)</td>
</tr>
<tr>
<td>Source gas flow rate</td>
<td>177 cc/min</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>4 liters/min</td>
</tr>
<tr>
<td>Total reaction pressure</td>
<td>1 atm</td>
</tr>
<tr>
<td>Reaction temperature</td>
<td>600 °C</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>67 nm/min</td>
</tr>
</tbody>
</table>
mixed to form a dilute mixture of 0.42 vol.\% SiH\textsubscript{4} in He at a flow rate of 4.2 liters/min.

**Back Etching**

Silicon deposition occurs on all sides of the substrate. The film deposited on the back surface of the substrate lacks uniformity owing to its contact with the susceptor and is thus presumed not to interfere with the thickness monitoring of the front surface. It cannot be ignored, however, in reflection and transmission measurements, in which magnitudes as well as phases are important. Therefore the back surface Si layer was etched off using a solution of HF(50 vol.\%) + HNO\textsubscript{3}(50 vol.\%) applied with a cotton-tipped applicator. A small amount of front surface silicon was also etched in this manner from one corner of the substrate to make the film side of the substrate readily identifiable.

**Post-Deposition Hydrogenation**

Hydrogenation System

The hydrogenation reactor used in this study evolved from a system built by the Solar Energy Group to prepare black molybdenum thin films for photothermal conversion devices (Carver, 1980). The modifications have been extensive, however, so it is now very well suited to its hydrogenation application. Figure 5.2 is a schematic diagram of the reactor. Not shown is the Plexiglas cover that encloses the chamber for safety. The cover also contains two fans, which were used to cool the chamber after deposition.
Figure 5.2. Schematic Diagram of the Hydrogenation System.

- Pneumatic valve
- Mechanical valve
- Rotameter
For hydrogen to diffuse into a-Si, it must be in monatomic form. Hydrogen is atomized in a glow discharge just as silane molecules are broken apart in the GD deposition technique. In our system, the glow discharge is produced by an rf electromagnetic field. The field is produced inductively by a water-cooled 12-turn coil, 13 cm in diameter and 16 cm long (see Figure 5.5, page 58). The coil is formed from copper tubing 6 mm in diameter. Power to the coil is supplied by a Lepel (New York, N.Y.) induction heating generator (model T-2.5-1-KC1-B3W). Both the field strength and the frequency are adjustable.

A Welch (Skokie, Ill.) mechanical vacuum pump (model 1397) reduces the pressure in the chamber to allow a glow discharge. The pressure during hydrogenation is monitored by two Hastings-Raydist (Hampton, Va.) vacuum gauge tubes (type DV-3M); one gauge is placed at the inlet and one at the outlet of the chamber. An additional gauge is used at the inlet to monitor near atmospheric pressures during backfilling with argon (see Table 5.3, page 60).

The susceptor was constructed locally of Grade A Lava (from the 3M Company); it has been described by Schay (1981). Its most important property is that it is not heated by the rf field. Susceptor heating is accomplished by four Watlow (St. Louis, Mo.) Firerods (model GJJ63) powered by a variable ac transformer (Variac). In this manner, the temperature of the sample and the rf field strength can be adjusted independently.

The temperature of the susceptor is monitored by a type K (Chromel-Alumel) thermocouple inserted into a hole in the susceptor.
The susceptor surface temperature was calibrated against the temperature measured by the thermocouple by placing a second thermocouple on the surface in the center of the susceptor (Schay, 1981). In addition to calibration error, there was the problem of stabilizing the temperature at a desired value. The lag time between Variac adjustment and effect on measured temperature was greater than a minute, causing the actual substrate temperature to vary with time during hydrogenation. Its maximum deviation from the reported value, taking into account both calibration error and measured deviation, was about 16°C.

The chamber itself is made of quartz with a brass end plate at the outlet. The inner diameter of the chamber is 10.2 cm and the outer diameter is 10.7 cm so as to nearly fill the rf coil. The end plate is fitted with a compression sealed O-ring to connect with the gas outlet line and two feedthroughs, allowing electrical connection to the Firerods and thermocouple. The end plate is situated 14 cm from the closest coil turn and 22 cm from the sample. It is thus expected to have some effect on the electromagnetic field.

The susceptor and quartz sled are designed so that the sample sits near the radial center of the chamber, which is concentric with the coil. The samples were placed at the longitudinal center of the coil.

**Rf Generator Calibration**

Previous reports from the Solar Energy Group have given the rf field strength only in relative units corresponding to a dial setting on the generator. There is no way to determine the resulting field
strength from the gauges on the generator. Nor was the precise frequency of the generator known; its range is given as 250 to 800 kHz. Therefore an oscilloscope (Gould, Cleveland, Ohio, model OS-260) was used to display the voltage across the coil as a function of time so as to derive both the field strength and the frequency. Owing to the magnitude of the expected voltages, it was necessary to use a ×1000 attenuating probe (Tektronix, Beaverton, Ore., model P 6013A) between the coil and the oscilloscope.

The results for the relative dial setting 27.5, used exclusively in this thesis, are shown in Figures 5.3 and 5.4. Figure 5.3 shows the pattern observed on the oscilloscope with a sweep rate of 0.5 μs/div. Each sweep shows a voltage oscillating with frequency 400 kHz, but the amplitudes of the individual sweeps are variable. Figure 5.4 shows the pattern observed on the oscilloscope with a sweep rate of 2 ms/div. The amplitude modulation is clearly seen in this figure and has a frequency of 120 Hz. The vertical scale in both figures, accounting for the ×1000 attenuation, is 500 V/div. The absolute maximum voltage measured, V_m, is 1.75 kV. A complete accounting of voltage vs. dial setting is not given because of changes that have since been made in the rf generator.

The instantaneous, spatially averaged, electric field strength in the azimuthal direction at the radial boundary of the coil is calculated by dividing the observed voltage by the total path length along the coil (490 cm). The wave equation for the electric field vector, \( \mathbf{E} \), is
Figure 5.3. Voltage Across Rf Coil vs. Time, 500 V/div Vertical, 0.5 μs/div Horizontal.
Figure 5.4. Voltage Across Rf Coil vs. Time, 500 V/div Vertical, 2 ms/div Horizontal.
\[ \nabla \times \nabla \times \mathbf{E} + \varepsilon_0 \mu_0 \frac{\partial^2 \mathbf{E}}{\partial t^2} = 0. \]

If the coil were infinitely long, we could solve for \( \mathbf{E} \) assuming \( \mathbf{E}(r,t) = \mathbf{E}_0(\rho)\cos(\omega t)\hat{\phi} \), where \( \rho \) is the radial coordinate, \( t \) is time, and \( \hat{\phi} \) is the azimuthal unit vector (see Figure 5.5). The result is \( \mathbf{E}_0(\rho) = J_1(\omega \rho / c) \), where \( J_1 \) is the first order Bessel function of the first kind.

In our case, \( \omega = 2.5 \times 10^6 \text{ sec}^{-1} \) and \( \rho_{\text{max}} = R \) = radius of coil = 6.5 cm. Hence, \( \frac{\omega R}{c} = 5.4 \times 10^{-4} \), and only the lowest term in the expansion of \( J_1 \) need be retained. To lowest order, \( J_1(\omega \rho / c) \approx \rho \). Although our coil is not infinitely long, it is not unreasonable to assume that the electric field strength inside it increases from 0 at the center to its measured value at the coil boundary in an approximately linear fashion.

The above analysis ignores the overall amplitude modulation shown in Figure 5.4. Let us represent this modulation by a function \( F(t) \) and write

\[ \mathbf{E}(r,t) = \mathbf{E}_0(\rho) F(t) \cos(\omega t) \hat{\phi}. \]

We approximate \( \mathbf{E}_0(\rho) \) assuming linearity in \( \rho \) and write

\[ \mathbf{E}(r,t) = \frac{\rho}{R} E_m F(t) \cos(\omega t) \hat{\phi}, \]

where
Figure 5.5. Coil Geometry.

(a) Side view
(b) End view
\[ E_m = \frac{V_m}{490 \text{ cm}} = \text{absolute maximum electric field strength.} \]

We approximate \( F(t) \) from Figure 5.4 as

\[
F(t) = \begin{cases} 
1 - \frac{t}{\tau} & \text{if } 0 < t < \tau \\
0 & \text{if } \tau < t < P 
\end{cases}
\]

, periodic with period \( P = 8.33 \text{ ms} \).

The root mean square electric field is given by

\[
E_{\text{rms}}(\rho) = \frac{\rho}{R} E_m \left[ \frac{1}{P} \int_0^P F^2(t) \cos^2(\omega t) dt \right]^{1/2}.
\]

Using the fact that \( \cos(\omega t) \) varies much faster than \( F(t) \), we get

\[
E_{\text{rms}}(\rho) = \left( \frac{\tau}{6P} \right)^{1/2} \frac{\rho}{R} E_m.
\]

Both \( E_m \) and \( \tau \) vary with the rf dial setting, while \( P \) and \( R \) remain constant.

Procedure

The procedure used to hydrogenate the samples is given in Table 5.3. \( \text{H}_2 \) is the only gas intentionally in the chamber while the rf field is on.

Since the field is left on during cooldown, we expect the front surface of the film to have a greater concentration of hydrogen, with respect to the bulk, than would be predicted by a complementary
Table 5.3. Hydrogenation Procedure

1. Purge the system with argon at atmospheric pressure for at least 3 minutes.
2. Pump down.
3. Start heating.
4. Backfill with argon to near atmospheric pressure and pump it out again. Repeat once.
5. Continue low pressure argon purge.
6. Close off argon and open hydrogen; set desired flow rate and pressure.
7. Turn the rf generator on to the desired setting when the temperature is near the desired value. Hydrogenation begins at this point.
8. Turn the heaters off and the cooling fans on after the desired time interval.
9. Turn the rf generator off when the temperature has fallen to 200 C. At this point hydrogenation ends.
10. Close off hydrogen and open argon; purge at low pressure.
11. Open the chamber to atmosphere when the temperature is less than 50 C.
error function profile (see Chapter 3). Temperatures of less than 170°C could not be measured reliably with the rf field on, owing to the heating of the thermocouple sheath by the field. The Firerods were also heated by the field, making temperatures of less than 170°C hard to achieve with the field on (Schay, 1981). We therefore turned the field off at 200°C rather than room temperature. No hydrogen evolution is expected below 200°C (Fritzsche, 1977).

Parameters

The results of two hydrogenation runs are reported in this thesis. One, at 400°C, was performed by the writer and the other, at 500°C, by Peter Hey. One sample of each thickness was included in each run. All hydrogenation parameters other than temperature were the same for both runs and are given in Table 5.4. The reported electric field strengths are those that exist at the radial boundary of the coil as described above. For the relative rf dial setting of 27.5, $V_m = 1.75$ kV and $\tau = 1.7$ ms.

**Electrical Contacts**

Aluminum contacts were evaporated onto all samples prior to conductance measurement. Prior to contacting, the samples were rinsed with HF to remove any oxide layer that may have formed after deposition.

The evaporation was performed near room temperature (which avoids evolving hydrogen) at about $10^{-4}$ torr. The aluminum was evaporated by a resistance heated wire helix. The evaporation was allowed to continue until the contacts were opaque (about 100 nm thick).
Table 5.4. Hydrogenation Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working gas</td>
<td>H₂</td>
</tr>
<tr>
<td>Flow rate</td>
<td>40 cc/min</td>
</tr>
<tr>
<td>Pressure</td>
<td>~0.3 torr</td>
</tr>
<tr>
<td>Relative rf dial setting</td>
<td>27.5</td>
</tr>
<tr>
<td>Maximum electric field strength at coil (Eₘ)</td>
<td>3.6 V/cm</td>
</tr>
<tr>
<td>RMS field strength at coil (Eₑₚₛ (R))</td>
<td>0.66 V/cm</td>
</tr>
<tr>
<td>Frequency (ω/2π)</td>
<td>400 kHz</td>
</tr>
<tr>
<td>Time from rf generator on (step 7 of Table 5.3) to heaters off (step 8)</td>
<td>30 min</td>
</tr>
</tbody>
</table>
An aluminum mask, constructed by Rolf Schay (Schay, 1981), allowed the deposition of four contacts spaced 0.9 mm apart. The samples were fastened onto the mask prior to evaporation so that the sample regions that were to stay bare were in direct contact with the mask. By this method, uniform, equally spaced aluminum contacts were obtained on the films. Figure 5.6 is a photograph of the mask along with a contacted sample.
Figure 5.6. Contacting Mask and a Contacted Sample.
CHAPTER 6

OPTICAL MEASUREMENTS

Reflection and transmission measurements were performed on samples of each of the three thicknesses before and after hydrogenation to determine the effects of hydrogen on the optical constants of the films. The instruments and procedures used to take these measurements are described below, followed by a discussion of the method used to derive the optical constants.

Where the distinction is important, the term "transmission" is used to refer to the result, in arbitrary units, of a single measurement. "Transmittance," on the other hand, refers to the ratio of intensity of transmitted light to that of incident light. "Reflection" and "reflectance" are similarly defined.

The Spectrophotometer

The instrument used to measure the reflectance and transmittance of the samples reported in this work was a Cary Instruments (Monrovia, Calif.) Spectrophotometer (model 14), commonly and henceforth referred to as the "Cary 14".

The Cary 14 may be operated in one of three modes: ultraviolet (UV), visible, and infrared (IR). Although reflectance and transmittance were measured for wavelengths as low as 440 nm, the IR mode was used exclusively so as to permit continuous scanning of all wavelengths of interest in a single run without changing modes. The IR
source lamp was strong enough throughout the measured wavelength range that the slit width, which is automatically adjusted for variations in reference beam signal, was always less than 0.2 mm.

Figure 6.1 is a diagram of the Cary 14 optics in the IR mode. Light from the tungsten lamp (Y) is split by the mirrors (W,W') and passes through a reference chamber and sample chamber. Light from each of the chambers is alternately sent to the monochromator by means of a semicircular rotating mirror (O) and chopper (N). The monochromator consists of a 600-line/mm echelette grating (J) in series with a $30^\circ$ fused silica prism (F). The monochromatic light is then sent to a PbS cell (f) for detection.

By a series of photometric circuits, reference and sample signals are stored as capacitor voltages. A 60-Hz chopper relay compares the voltages stored on the two capacitors and, if they are not equal, generates a 60-Hz signal that causes the recorder pen amplifiers and motor to readjust the recorder slidewire to balance the reference and sample signals. (See the Cary 14 operating manual for further details.)

The Cary 14 is equipped with a balance control that can be used to adjust the relative attenuation of the sample and reference beams. An "upward" adjustment of the balance control results in a larger transmission (or reflection) reading.

Transmission

Owing to the small size of the samples (0.480 x 0.350 in.), it was necessary to design a special sample holder for transmission
Figure 6.1. Diagram of the Cary 14 Optical System in the IR Mode.
measurements. The holder was machined from aluminum and subsequently blackened by anodization to reduce stray reflections. Its window is 0.360 x 0.200 in., oriented vertically.

Nothing is used in the reference chamber for transmission measurements.

Reflection

Our Cary 14 is equipped with a reflection attachment (model 1413), which is placed in the sample chamber for reflection measurements. Figure 6.2 is a diagram of the optics of this attachment. Light enters the attachment and is reflected by three aluminum mirrors, the last of which (M₃) focuses the light on the sample (S₁) with an 8° angle of incidence. Light reflected from the sample is focused by a fourth mirror (M₄) onto a second point on the sample (S₂) with the same angle of incidence. The reflected light is focused by a fifth mirror (M₅) and undergoes two more reflections before being focused by a lens (L) and exiting the sample chamber. For reference, a sample having 100% reflectance is simulated by moving the mirror at M₄ to position M₄' and removing the sample.

The samples were too small to reflect light from more than one spot at the same time. Therefore, a sample holder had to be designed to fit into the reflection attachment which would hold two samples. The holder was made of blackened aluminum, like the transmission sample holder, with two vertically oriented 0.360 x 0.200 in. windows. It was designed to leave all of the optical path lengths and angles of the original attachment unaltered.
Figure 6.2. Diagram of the Cary 14 Specular Reflection Attachment.
The light getting through the reflection attachment is greatly attenuated by its seven mirrors. Since the range of balance control is too narrow to compensate them, it is necessary to place a beam attenuator in the reference chamber for reflection measurements. The attenuator is a black louver comb provided by Cary. The attenuation is adjusted by rotating the comb with respect to the reference beam.

**Computer Data Collection System**

The chart recorder pen location on the Cary 14 is read by a position encoder, constructed by Michael Jacobson and Riley Puckett, consisting of a potentiometer and a seven-bit A/D converter. The data are fed into a microcomputer (Southwest Technical Products, San Antonio, Tex., model 6800), which is interfaced with a floppy disk drive (Siemens, Iselin, N.J., model FDD 100-8D) for data storage. In addition to the actual measurement, the computer receives from the Cary a wavelength marker every 10 nm.

The software used in the data collection was written by Johann Pramberger. It causes the computer to record a measurement at each wavelength marker as well as at user-selected time intervals.

**Procedure**

Transmittance and/or reflectance was measured for wavelengths ranging from 440 to 2500 nm. At 440 nm all samples were opaque, while in the 1000 to 2500 nm range all samples were transparent. Henceforth, the absorption edge range, 440 to 900 nm, will be referred to as the "visible" and the range 1000 to 2500 nm will be referred to as the "near infrared" (NIR). The computer data collection system was used
for all visible traces. In the NIR, the chart recorder output was digitized by hand and entered on the terminal keyboard for subsequent analysis. Data recorded directly by the computer has a resolution 1/256 full scale; the chart recorder output can be resolved to 1/500 full scale.

Although reflection and transmission measurements were ultimately extracted only at 10-nm intervals, the computer recorded data every nanometer as determined by the timing device in the program. This was necessitated by the occasional occurrence of a false wavelength marker, that is, a wavelength marker received but never sent. Fortunately, there was never a problem with markers being sent but not received. False markers could therefore be picked out of the data by counting the data points collected between successive markers.

Transmittance

The transmittance of all samples was measured in the visible and the NIR. A 100% line was taken first with the empty sample holder in place. Then the samples to be measured were blown clean with dry nitrogen, placed successively in the holder, and their transmissions recorded. Samples were placed in the holder film side down with the corner of the substrate not covered with film (see Chapter 5, "Back Etching") residing totally outside the window. Light was incident from the substrate side. Afterward, a second 100% line was taken to check that the optics had not been altered. The observed 100% line drift was less than 2% for transmission measurements.
Reflectance

The procedure for measuring reflectance was more involved than for transmittance owing to the necessity of using the reflection attachment and accompanying beam attenuator described above. Two samples were required to measure reflection. In all cases, the second "sample" was an aluminum mirror deposited on a quartz substrate in the same system used to deposit electrical contacts as described in Chapter 5. This mirror will be called a "dummy sample" or "dummy" to distinguish it from the other mirrors in the system. The reflectance of the dummy was measured for each reflectance run using two dummies that had been deposited simultaneously.

In addition to front reflectance, the back reflectance of some samples was measured in hopes of facilitating the extraction of the optical constants as described below. "Front reflectance" indicates the light is incident from the film side whereas "back reflectance" indicates the light is incident from the substrate side. Referring to Figure 6.2, front reflection was measured with the sample in position $S_2$ and the dummy in position $S_1$, whereas for back reflection the positions were reversed. In this manner both reflections are measured on the same spot on the sample even though it has been turned over.

Since two dummies must be measured to derive the reflectance of each, no loss of consistency resulted from using a separate dummy for front and back reflection. Thus, some dummies were designated to be used only at $S_1$ and others only at $S_2$. In this manner, scratches that may have appeared on a dummy owing to its contact with the sample holder were never on the measured part of the dummy.
The procedure used to measure reflectance is summarized in Table 6.1. The first column describes the measurement taken, and the second and third columns specify the object in positions \( S_1 \) and \( S_2 \) respectively (see Figure 6.2). Reflectance was measured only in the visible. Prior to measurement, samples and dummies were blown clean with dry nitrogen.

After a 100% line and a dummy-dummy trace are taken, the reflectance of the dummies may be calculated. Since we now have a reference of known reflectance, we may, if we wish, readjust the balance upward for greater accuracy. Although the new balance may put the 100% line off scale, we need never return to it.

When all the sample traces were complete, a final reference trace was taken. A "reference" trace is a 100% line or a dummy-dummy reflection, depending on whether the balance was readjusted after the first dummy-dummy reflection. In some runs, a reference trace was taken between the front and back sample traces. Reference line drift was difficult to control during reflection measurements, probably because of inadvertent scratches on the dummies or the great sensitivity of such measurements to beam attenuator orientation. If the reference trace drift was greater than 3% during front reflection measurements, all traces were repeated. For drifts less than 3%, various objective and subjective means were tried in order to decide how to weigh each trace to get an average reference trace.
Table 6.1. Reflectance Measurement Procedure

<table>
<thead>
<tr>
<th>Trace</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%</td>
<td>empty</td>
<td>empty</td>
<td>Mirror in position $M_4'$</td>
</tr>
<tr>
<td>Dummy reflection</td>
<td>dummy</td>
<td>dummy</td>
<td>Balance readjusted upward; not done in all runs</td>
</tr>
<tr>
<td>Dummy reflection</td>
<td>dummy</td>
<td>dummy</td>
<td>If balance was readjusted</td>
</tr>
<tr>
<td>Front reflections</td>
<td>sample</td>
<td>dummy</td>
<td>All samples measured successively</td>
</tr>
<tr>
<td>Dummy reflection</td>
<td>dummy</td>
<td>dummy</td>
<td>Not done in all runs</td>
</tr>
<tr>
<td>Back reflections</td>
<td>dummy</td>
<td>sample</td>
<td>All samples measured successively</td>
</tr>
<tr>
<td>Dummy reflection</td>
<td>dummy</td>
<td>dummy</td>
<td>If balance was readjusted</td>
</tr>
<tr>
<td>100%</td>
<td>empty</td>
<td>empty</td>
<td>If balance was not readjusted; mirror in position $M_4'$</td>
</tr>
</tbody>
</table>

See text for explanation.
Calculations

Notation

To discuss the reflectance and transmittance of a thin film on a substrate, it is necessary to consider many individual reflectances and transmittances from the various interfaces, bulk films, and combinations thereof. Therefore a general notation is adopted, for use in this chapter only, to denote these reflectances and transmittances, as follows:

Let all the media through which the light must travel to be transmitted through the tandem be labeled sequentially 0, 1, 2, 3, ..., N, where 0 refers to air before the first film and N refers to air after the last film. Each label from 1 to N−1 represents a film in the tandem; it makes no difference (to the notation) whether the films are thin or thick. The various reflection and transmission coefficients as well as thickness and complex index of refraction are subscripted to denote the media they relate to, as defined in Table 6.2. Figure 6.3 will help to clarify these definitions. If a symbol for reflectance or transmittance is not superscripted, it will refer to a "theoretical" value calculated from the appropriate indexes of refraction. Symbols referring to measured quantities will be superscripted with an M. Normal incidence will be assumed at all times.

Thermodynamic considerations require that $T_{ji} = T_{ij}$.

If medium $i$ is transparent ($k_i = 0$), we have

$$R_{ij} = |r_{ij}|^2.$$  \hspace{1cm} (1a)
Table 6.2. Thin Film Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>Wavelength of the light in air</td>
</tr>
<tr>
<td>$\tilde{n}_i$</td>
<td>Complex index of refraction of medium $i$</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>Thickness of medium $i$ ($i = 1, 2, 3, \ldots, N-1$)</td>
</tr>
<tr>
<td>$t_i$</td>
<td>Internal amplitude transmittance through medium $i$</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Internal energy transmittance through medium $i$</td>
</tr>
<tr>
<td>$t_{ij}$</td>
<td>Amplitude transmittance of light from medium $i$ to medium $j$</td>
</tr>
<tr>
<td>$r_{ij}$</td>
<td>Amplitude reflectance complementary to $t_{ij}$</td>
</tr>
<tr>
<td>$T_{ij}$</td>
<td>Energy transmittance of light from medium $i$ to medium $j$</td>
</tr>
<tr>
<td>$R_{ij}$</td>
<td>Energy reflectance complementary to $T_{ij}$</td>
</tr>
</tbody>
</table>
Figure 6.3. Transmission and Reflection.

a. Interface between two media
b. Thin film between two semi-infinite media
c. Thin film (Medium 1) on a substrate (Medium 2)
If both media i and j are transparent, we have

\[ T_{ij} = \frac{n_j}{n_i} |t_{ij}|^2. \]  

(1b)

If i and j share a common interface (j = i+1 or i-1), we have the Fresnel relations for normal incidence:

\[ r_{ij} = \frac{n_i - \tilde{n}_i}{n_i + \tilde{n}_j}, \]
\[ t_{ij} = \frac{2n_i}{n_i + n_j}. \]  

(2)

If medium i is a thin film (a film that shows fringe effects), its internal amplitude transmittance may be written:

\[ t_i = \exp\left(-\frac{-12\pi \tilde{n}_i \tau_i}{\lambda}\right) = \exp\left(-\frac{-2\pi k_i \tau_i}{\lambda}\right) \exp\left(-\frac{-12\pi n_i \tau_i}{\lambda}\right). \]  

(3)

In the present case of a single thin film of a-Si on sapphire, there are four media: 0 is air, 1 is a-Si, 2 is sapphire, and 3 is air.

Calculation of Measured Quantities from the Film Index

To calculate the optical constants and thickness of a thin film on a substrate, we must be able to calculate the functions \( T_{03}(n_1,k_1,\lambda,\tau_1,n_2) \), \( R_{03}(n_1,k_1,\lambda,\tau_1,n_2) \), and \( R_{30}(n_1,k_1,\lambda,\tau_1,n_2) \), which give the normal incidence transmittance, front reflectance, and back reflectance, respectively, of the film/substrate tandem in terms of
the complex index of refraction of the film, \( n_1 = n_1 - ik_1 \); the wavelength of the incident light, \( \lambda \); the thickness of the film, \( t_1 \); and the index of refraction of the substrate, \( n_2 \) (see Figure 6.3). We assume that \( n_0 = n_3 = 1 \).

For transmission measurements at wavelengths above 2.3 \( \mu m \), minute fringes were observed that were attributable to the substrate. Although the substrate will always be considered a thick film (a film that shows no fringe effects), the observation of fringes demonstrates that its faces are very plane parallel. We must therefore account for reflection from the back surface of the substrate by summing as shown in Figure 6.3c. Since the substrate is thick, it is the energy reflections and transmissions that must be summed. Furthermore, the substrate is transparent for all wavelengths of concern to this study. The overall transmittance and reflectance of the substrate/film tandem are thus given by

\[
T_{03} = \frac{T_{02}T_{23}}{1 - R_{20}R_{23}}
\]

\[
R_{03} = R_{02} + \frac{T_{02}R_{23}}{1 - R_{20}R_{23}}
\]

\[
R_{30} = R_{32} + \frac{T_{23}R_{20}}{1 - R_{20}R_{23}}
\]

\( T_{23}, R_{23}, \text{ and } R_{32} \) may be calculated from equations (1) and (2) if the substrate index is known. To calculate \( T_{02} \), we sum the contributions of all the reflections inside the film as shown in Figure 6.3b. Since the film is thin, we must sum the amplitudes. The result is
\[ t_{02} = \frac{t_{01}t_{12}l_1}{1 - r_{10}r_{12}l_1^2} \]
\[ r_{02} = r_{01} + \frac{t_{01}r_{10}r_{12}l_1^2}{1 - r_{10}r_{12}l_1^2} \]
\[ r_{20} = r_{21} + \frac{t_{21}r_{12}l_1l_2}{1 - r_{10}r_{12}l_1^2}. \]

(5)

\[ T_{02}, R_{02}, \text{and } R_{20} \text{ are then obtained from equation (1).} \]

All the terms on the right-hand side of equations (5) may be found from equations (2) and (3). The result must then be converted to real-valued form for BASIC language computer computation. The result of this analysis for \( T_{02} \) and \( R_{02} \) (Heavens, 1964, p. 208) is given in Table 6.3. \( R_{20} \) may be found by exchanging \( n_0 \) and \( n_2 \).

**Film Thickness**

If the film is transparent \( (k_j = 0) \) and of greater index than the substrate, its thickness may be calculated by observing a transmittance minimum. For \( k_j = 0 \), the above equations reduce to

\[ T_{03}(n_1, 0, \lambda, \tau_1, n_2) = \left\{ \frac{K^2}{4n_2^2} - 1 + \frac{1}{8n_1n_2} \left[ \frac{n_1^4}{n_1} + (2n_2 + K^2)n_1^2 \right] \right. \]
\[ + \left. n_2^2 - \left( n_1^4 + (2n_2 - K^2)n_1^2 + n_2^2 \right) \cos\left( \frac{4\pi n_1 \tau_1}{\lambda} \right) \right\}^{-1}, \]

(6)

where \( K = n_2 + 1 \). We may factor the coefficient of \( \cos(4\pi n_1 \tau_1/\lambda) \) as follows:
Table 6.3. Calculation of Functions $T_{02}(n_0,n_1,k_1,\lambda,\tau_1,n_2)$ and $R_{02}(n_0,n_1,k_1,\lambda,\tau_1,n_2)$

Let

\[
\begin{align*}
    n' &= n_1/n_0 \\
    k' &= k_1/n_0 \\
    n'_2 &= n_2/n_0
\end{align*}
\]

\[
\begin{align*}
    A &= (n'^2+k'^2+1)(n'^2+k'^2+n'_2) - 4n'^2n'_2 \\
    B &= 2n'[n'_2(n'^2+k'^2+1)-(n'^2+k'^2+n'_2)] \\
    C &= (n'^2+k'^2-1)(n'^2+k'^2-n'_2) + 4k'^2n'_2 \\
    D &= 2k'[n'_2(n'^2+k'^2-1)-(n'^2+k'^2-n'_2)] \\
    E &= (n'^2+k'^2+1)(n'^2+k'^2+n'_2) + 4n'^2n'_2 \\
    F &= 2n'[n'_2(n'^2+k'^2+1)+(n'^2+k'^2+n'_2)] \\
    G &= (n'^2+k'^2-1)(n'^2+k'^2-n'_2) - 4k'^2n'_2 \\
    H &= 2k'[n'_2(n'^2+k'^2-1)+(n'^2+k'^2-n'_2)]
\end{align*}
\]

\[
\begin{align*}
    \sigma &= 4\pi k_1\tau_1/\lambda \\
    \zeta &= 4\pi n_1\tau_1/\lambda
\end{align*}
\]

Then

\[
T_{02} = \frac{8n'_2(n'^2+k'^2)}{E \cosh \sigma + F \sinh \sigma - G \cos \zeta + H \sin \zeta}
\]

and

\[
R_{02} = \frac{A \cosh \sigma + B \sinh \sigma - C \cos \zeta + D \sin \zeta}{E \cosh \sigma + F \sinh \sigma - G \cos \zeta + H \sin \zeta}
\]
\[ n_1 + (2n_2 - k^2)n_1^2 + n_2^2 = (n_1 + n_2)(n_1 + 1)(n_1 - n_2)(n_1 - 1). \]

Therefore, assuming \( n_1 > n_2 \), \( T(n_1, k_1, \lambda, \tau_1, n_2) \) is minimum with respect to \( \lambda \) where \( \cos(4\pi n_1 \tau_1 / \lambda) = -1 \), or

\[ 2n_1 \tau_1 = m \lambda_{\text{min}}, \quad m = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots, \quad (7) \]

where \( \lambda_{\text{min}} \) denotes the wavelength at which the minimum in \( T_{03} \) is observed. Using equation (7) in equation (6),

\[ T_{03}(n_1, 0, \lambda_{\text{min}}, \tau_1, n_2) = \frac{4n_1^2 n_2}{(n_1^2 + 1)(n_1^2 + n_2^2)}. \quad (8) \]

Hence, by measuring \( T_{03} \) and knowing \( n_2 \), we may solve for \( n_1 \).

If we already have an approximate value of \( \tau_1 \), as we do from the deposition thickness monitor, we can solve for \( \tau_1 \) by finding the closest \( \tau_1 \) to the approximate one that satisfies equation (7).

Optical Constants

The equations \( T_{03}(n_1, k_1, \lambda, \tau_1, n_2) = T_{03}^M \) and \( R_{03}(n_1, k_1, \lambda, \tau_1, n_2) = R_{03}^M \), where \( T_{03}^M \) and \( R_{03}^M \) are the measured transmittance and front reflectance respectively, have not been inverted analytically to derive \( n_1 \) and \( k_1 \). It is therefore necessary to find the solutions numerically. To do this, we define a function
\[ \chi^2(n_1, k_1; \lambda, \tau_1, n_2) = [1 - \frac{T_{\lambda 3}(n_1, k_1, \lambda, \tau_1, n_2)}{T_{\lambda 3}^M}]^2 + [1 - \frac{R_{\lambda 3}(n_1, k_1, \lambda, \tau_1, n_2)}{R_{\lambda 3}^M}]^2. \]

Here \( n_1 \) and \( k_1 \) are considered to be the variables of the function \( \chi^2 \) and \( \lambda, \tau_1, \) and \( n_2 \) are known input parameters. In the future, we will drop the parameters \( \tau_1 \) and \( n_2 \) and identify

\[
\begin{align*}
n &= n_1 \\
k &= k_1.
\end{align*}
\]

We then write simply \( \chi^2(n, k; \lambda) \). A "solution" will be defined to exist at any local minimum of the function \( \chi^2(n, k; \lambda) \) with respect to \( n \) and \( k \). A "solution branch" or "branch" will refer to a series of solutions for different \( \lambda \) that appear to be connected to each other by nearness of the various \( n \)'s and \( k \)'s and/or constancy of \( \Delta n/\Delta \lambda \) and \( \Delta k/\Delta \lambda \).

The values of the parameters are determined as follows: \( \lambda \) is given by the Cary 14; \( n_2 \) is calculated from the dispersion relation for sapphire (Wolfe, 1978, p. 7-101); \( \tau_1 \) is determined from transmission minima in the NIR (in the case of samples from the two thicker series) or from the deposition thickness monitor (in the case of the thinnest samples for which no NIR transmission minima could be observed).

The writer first attempted to solve for \( n \) and \( k \) using a "guess-and-revise" algorithm. Starting with guesses for \( n \) and \( k \) at a given wavelength as inputs, an attempt was made to find the solution closest to the given guesses. The solution thus found became the
guess for the next wavelength, and so on. After a few wavelengths, this algorithm failed to give reasonable values of \( n \) and \( k \).

After giving up on the guess-and-revise algorithm, the author went to an exhaustive search algorithm. This program reported all solutions found in a given range of \( n \) and \( k \), \( n_L < n < n_H \) and \( k_L < k < k_H \). Unfortunately, we cannot actually calculate \( \chi^2(n,k;\lambda) \) for all \( n \) and \( k \) inside any range, and we must divide the range up into a discrete grid. Therefore, grid numbers \( N_n \) and \( N_k \) were defined, which indicate the number of discrete steps taken over the \( n \) range and \( k \) range respectively. Table 6.4 gives each wavelength range searched, together with the \( n_L, n_H, N_n, k_L, k_H \), and \( N_k \) used. The shortest wavelength analyzed depended on sample thickness.

Although back reflectance (\( R_{03} \)) was measured for most samples, it was not included in the computation of \( \chi^2(n,k,\lambda) \) during the search for solutions. It was originally hoped that the inclusion of \( R_{30}^M \) would help identify false solutions. This was not the case, however; all solutions found without \( R_{30}^M \) resulted in \( \chi^2 \) values less than \( 2 \times 10^{-3} \) when \( R_{30}^M \) was included. Its principal utility was to check the accuracy of the optical measurements.

Although the values of \( n \) reported in the literature for a-Si vary, they all show negative \( dn/d\lambda \) above 490 nm. This fact turned out to be the most valuable tool in selecting the correct solution branch. Typically, only one branch had negative \( dn/d\lambda \).

---

1. If \( k_L = 0 \), the program also reported local minima at \( k = 0 \).
### Table 6.4. Exhaustive Search Parameters

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>$n_L$</th>
<th>$n_H$</th>
<th>$N_n$</th>
<th>$k_L$</th>
<th>$k_H$</th>
<th>$N_k$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>440 - 480</td>
<td>3</td>
<td>7</td>
<td>128</td>
<td>0.5625</td>
<td>1.25</td>
<td>256</td>
<td>Shortest wavelength analyzed varies with sample thickness</td>
</tr>
<tr>
<td>500 - 580</td>
<td>3</td>
<td>7</td>
<td>128</td>
<td>0.25</td>
<td>0.75</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>600 - 660</td>
<td>3</td>
<td>7</td>
<td>128</td>
<td>0</td>
<td>0.5 or 0.375</td>
<td>256</td>
<td></td>
</tr>
<tr>
<td>680 - 720</td>
<td>2</td>
<td>6</td>
<td>128</td>
<td>0</td>
<td>0.25 or 0.1875</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>740 - $\lambda_T$</td>
<td>2</td>
<td>6</td>
<td>128</td>
<td>0</td>
<td>0.125 or 0.0625</td>
<td>128</td>
<td>$740 &lt; \lambda_T &lt; 840$ depending on sample thickness</td>
</tr>
<tr>
<td>$\lambda_T$ - 2500</td>
<td>2</td>
<td>6</td>
<td>1024</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Film Inhomogeneity

For the analysis discussed above, it was assumed that n and k were independent of depth into the film. This assumption is unjustified, however, when hydrogen is diffused into the material with an inhomogeneous concentration profile (see Figures 3.3 and 3.4). Furthermore, there is evidence that n is lower near the surface even for the as-deposited material. Kühl, Schlotterer, and Schwidefsky (1974) noted that a different value of n is obtained at nearly the same wavelength depending on whether it is calculated from interference fringes (which they presume to give an average value of n throughout the film) or from front surface reflectance (which they presume to give the surface index).

Owing to the thinness of the films and the resulting lack of fringes, the author had to use exact thin film equations to compute n and k. Since only front reflection was used in the computation of $\chi^2(n,k;\lambda)$, we might expect the resulting n and k to become more characteristic of the front surface (as opposed to the bulk) as $\lambda$ decreases and the film becomes more absorbing. We can test this hypothesis by including back reflection in the computation of $\chi^2(n,k;\lambda)$ once solutions for n and k have been found; the resulting $\chi^2$ values should increase with decreasing $\lambda$. This was not found to be the case, even for hydrogenated samples. We assume, therefore, that any variation in the optical constants with depth is small enough to be ignored in the computation of the front and back interface reflectances and transmittances, $r_{01}$, $r_{10}$, $r_{12}$, $r_{21}$, $t_{01}$, etc. That is, the same solution for n and k used to compute $r_{01}$ may be used to compute $r_{12}$, the results for
$R_{03}$ and $T_{03}$ being not significantly different from what they would have been had the actual values of $n$ and $k$ at each interface been used. Of course, the $n$ and $k$ used should lie somewhere between their respective extreme values.

Equations (1), (2), (3), and (5) produced the equations of Table 6.3. A close inspection of these equations reveals that all cases where $n$ and $k$ are not multiplied by the film thickness ($\tau_i$ or $\tau$) derive from the Fresnel relations at the film interfaces (equation 2). In these cases, specifically, in the computation of the coefficients $A$ through $H$, we can thus use any values of $n$ and $k$ between their respective extremes without significantly altering the results.

The cases where $n$ and $k$ are multiplied by $\tau$ derive from the internal transmittance given by equation (3). Since $n$ and $k$ appear there in exponents, small variations in their values may produce significant variations in the results. Ignoring internal reflections, the internal transmittance of a tandem of films $i$ and $j$ is given by

$$t_{i+j} = t_i t_j = \exp\left(\frac{-2\pi(k_i \tau_i + k_j \tau_j)}{\lambda}\right) \exp\left(\frac{-i2\pi(n_i \tau_i + n_j \tau_j)}{\lambda}\right).$$

Clearly, if we consider the film to have continuously varying optical constants $n(x)$ and $k(x)$, where $x$ is the depth into the film, we should replace $n\tau$ and $k\tau$ with $\int_0^\tau n(x)dx$ and $\int_0^\tau k(x)dx$ respectively. Therefore, defining the average $n$ and $k$ as
\[ \overline{n} = \frac{1}{\tau} \int_{0}^{\tau} n(x) \, dx \]

and

\[ \overline{k} = \frac{1}{\tau} \int_{0}^{\tau} k(x) \, dx, \]

we have, for a film of continuously varying index, that

\[ n \tau \text{ can be replaced by } \overline{n} \tau \]

and

\[ k \tau \text{ can be replaced by } \overline{k} \tau, \]

provided that variations in \( n \) and \( k \) are small enough to be ignored in the computation of interfacial reflectance and transmittance relations. Clearly, \( \overline{n} \) and \( \overline{k} \) lie between the extreme values of \( n(x) \) and \( k(x) \) respectively. They may thus be used in the computation of the coefficients \( A \) through \( H \) in Table 6.3 as described above.

One factor not yet considered is internal reflection; since the optical constants vary differentially with each differential of depth into the film, there will also be a differential internal reflection. We are, however, dealing with variations in \( n \) and \( k \) that are so small as to not result in much of a reflection even if they were abrupt. Their being continuous makes them even less of a problem, and we need not consider them further.

Having said all of this, it is reasonable to suppose that by measuring \( T_{03} \) and \( R_{03} \), and deriving an \( n \) and a \( k \), we will actually end up with \( \overline{n} \) and \( \overline{k} \) provided the variations in \( n \) and \( k \) meet the conditions described above.
CHAPTER 7

CONDUCTANCE MEASUREMENTS

To further evaluate the effects of post-deposition hydrogenation on the films, the conductances of samples of each of the three thicknesses were measured. Different samples were used for the as-deposited and the hydrogenated measurements. In this chapter, the instruments and procedures used to perform these measurements are described.

Four types of conductance will be distinguished: "Dark" conductance refers to conductance in the absence of any illumination. "White" conductance refers to the conductance while white light is normally incident on the film side of the sample. "Front blue" and "back blue" conductance refer to the conductances while blue light (2.3 eV < hν < 3.5 eV) is normally incident on the film side and on the substrate side of the sample respectively. The last three types of conductance fall into the category of "photoconductance".

Experimental Setup

Dark and white conductances were measured as a function of temperature from 150 to -150 C. If the films were exposed to the atmosphere at -150 C, water would condense on the sample surface; temperatures on the order of 150 C would favor diffusion of contaminants into the material. Therefore, all conductance measurements were performed under vacuum.
The vacuum was produced in two stages. A cryogenic sorption pump (Perkin Elmer, Ultek Division, model 236-1500) was used in the first step to obtain a rough vacuum (10⁻³ torr) before the high vacuum ion pump (Perkin Elmer, Ultek Division, model 202-2000) was turned on. Neither pump uses oil.

Figure 7.1 is a photograph of the sample chamber. The sample resides on a copper block (described below) behind a quartz window (A), which allows the sample to be illuminated. The chamber consists of two halves sealed together by a neoprene O-ring at (B). The sample is connected to the top half, which can be rotated to allow front or back illumination. Electrical connection to the interior of the chamber is made by means of copper wires that lead to the BNC type connectors at (C). The wires leading from the BNCs are soldered to standoffs in the sample holder as shown in Figures 7.2 and 7.3. The final connection to the sample is made by thin copper wires that are soldered to the standoffs and attached to the sample's aluminum contacts (see Figures 5.6 and 7.3) with Copper Print (GC Electronics, Rockford, Ill., catalog No. 22-208).

The sample holder is a nickel-plated copper block designed so that the axis of revolution (as the top half of the chamber is rotated) passes through the center of the sample. The sample was attached to the holder with high vacuum grease (Dow Corning, Midland, Mich.). The measured part of the sample resides over a slit in the holder that allows light to reach the sample during back blue conductance measurements. Figures 7.2 through 7.4 are photographs of the
Figure 7.1. Sample Chamber for Conductance Measurements.
Figure 7.2. Front View of Sample in Holder.
Figure 7.3. Closeup Front View of Sample in Holder.
Figure 7.4. Closeup Back View of Sample in Holder.
sample in the holder as seen from the front and back. Figure 7.5 is a horizontal cross section of the sample in the holder.

Heat to the sample is provided by two Firerods (Watlow, model 4979 E2A72) inserted into the sample holder from the top (see Figure 7.5). The holder is attached to a tube (see Figure 7.2) into which liquid nitrogen may be poured for sample cooling. Temperature was monitored by a platinum resistor (Omega Engineering, Stamford, Conn., model PT100 FKG 3/10) attached to the sample with high vacuum grease (see Figures 7.3 and 7.5) and connected to a digital readout (Omega Engineering, model 199).

Although the samples were contacted with four aluminum strips (see Figures 5.6 and 7.5), only two of the contacts were used to measure conductance. Figure 7.6 shows circuit diagrams for both two-point and four-point conductance measurements. The advantage of four-point measurements is that any contact resistances (by "contact resistance" is meant any non-ohmic Schottky barrier resistance as well as ohmic resistance) do not affect the measurement. The disadvantage of four-point measurements is that a voltmeter having an input resistance greater than the resistance of the sample must be used; this is a prohibitive consideration for sample resistance as great as $10^{15}$ Ω. Two-point measurements were also dictated in the present case by the back blue measurements. As seen in Figure 7.5, only the central resistor of Figure 7.6b would be illuminated from the back in a four-point configuration. Since resistance can decrease by more than a factor of 10 upon illumination (at room temperature), most of the voltage drop would be borne by the two outside resistors, reducing the accuracy of
Figure 7.5. Horizontal Cross Section of Sample in Holder.
Figure 7.6. Conductance Measurement Circuit Diagrams.

a. Two-point measurements
b. Four-point measurements
the measurement. The large resistance of the sample itself was assumed to render any contact resistance negligible.

The voltage, varied from 20 to 200 V, was supplied by a Kepco (Flushing, N.Y.) regulated dc supply (part 188-0030) and measured by a Fluke digital voltmeter (model 74095). Currents, ranging from $2 \times 10^{-13}$ to $5 \times 10^{-7}$ A, were measured by either a Keithley digital electrometer (model 642) or analog electrometer (model 610B). The electrometers were tested over a range of $10^{-11}$ to $10^{-7}$ A using a Victoreen standard resistor. The measured current was everywhere greater than the calculated; the maximum deviation was 16% of the measured value.

White measurements were performed with the quartz window uncovered and a Sylvania 500-W tungsten filament bulb (color temperature 3200 K) situated 19 cm from the sample. The photon flux incident on the sample as a function of photon energy is shown in Figure 7.7. It was calculated from the spectral radiant flux curves given in the SPSE handbook (Thomas, 1973, pp. 46-47) assuming that all 500 W are output as isotropic radiation and ignoring reflection losses from the window. Under these assumptions, the total irradiance at the sample is 110 mW/cm$^2$.

Blue measurements were performed with a filter (Rolyn Optics, Arcadia, Calif., stock No. 65.1135) over the window. The filter transmittance was measured on the Cary 14 and is shown in Figure 7.7. All samples were opaque over the pass band of the filter.
Figure 7.7. Photoconductance Source Spectra.

a. White spectrum of the tungsten lamp; after Thomas (1973)
b. Blue filter transmittance
Procedure

The procedure followed in the measurement of conductance is outlined in Table 7.1. A minimum of four days was required to measure each hydrogenated sample, covering pumpdown, dark conductance, white conductance, and blue conductance.

Before pumpdown, each sample was tested for linearity in the current vs. voltage characteristic and found to be linear from 1 to 200 V. Monitoring of the dark conductance was continued during heatup and pumpdown for comparison to high vacuum measurements. Dark conductance was observed to drop after pumpdown by a widely variable factor (1 to 20 times). Samples were allowed to remain in vacuum (<10^{-6} torr) for at least one day before measurement so as to release adsorbed gases more completely.

Hysteresis was checked for both dark and white conductance as described in Table 7.1. Hysteresis was less than 25% for both dark and photo measurements.

The pressure inside the chamber varied during the measurement cycle, being higher at higher temperatures. The minimum recorded pressure was 10^{-7} torr and the maximum was 10^{-5} torr.

Calculation of the Hydrogen Diffusion Constant from Blue Measurements

The advantage of using blue light (hv > 2.3 eV) to produce a photoconductance is that its penetration depth is very small. Only the thinnest samples (133 nm) had a measurable transmittance out to 2.3 eV. Using these samples, the absorption constant, \( \alpha = \frac{4\pi k}{\lambda} \), was
Table 7.1. Conductance Measurement Procedure

Day 1: Pumpdown

1. Attach contact wires and test.
2. Place sample in vacuum chamber and start dry nitrogen purge.
3. Cover window with aluminum foil.
4. Test current vs. voltage characteristic.
5. Start heating both sample and chamber.
6. When the sample temperature reaches 100 to 130°C and the chamber is at 100°C (1 to 4 hours after heating begins), start cryogenic sorption pumping.
7. When the sample temperature reaches 150 - 160°C, turn off all heaters.
8. Open the ion pump when outgassing has progressed sufficiently for continuous ion pumping to be maintained.

Day 2: Dark measurements

1. Heat sample to 150°C while measuring current for hysteresis check.
2. Cool sample to -150°C using liquid nitrogen. Measure current every 10°C down to -50°C and every 5°C thereafter. This procedure takes from 1.5 to 2.5 hours.
3. Allow sample to return to room temperature naturally.

Day 3: White measurements

1. Heat sample to 150°C while taking dark measurements.
2. Uncover window and turn lamp on.
3. Cool from 150°C to -150°C, using liquid nitrogen as before, taking white measurements (1 to 2 hours).
Table 7.1. Conductance Measurement Procedure (continued)

Day 3: White measurements (continued)

4. Take low temperature (-150 to -140 C) blue measurements as described below (as-deposited samples only).

5. Allow sample to heat to $= -100$ C with lamp on to check white hysteresis (not done with all samples).

6. Cover window with aluminum foil and allow to heat naturally to room temperature.

Day 4: Room temperature blue measurements (hydrogenated samples only)

1. Take a measurement with the sample covered (dark).

2. Remove the aluminum foil and place the blue filter over the window.

3. Take the front blue measurement.

4. Rotate the sample and take the back blue measurement.

5. Remove the blue filter and cover the window with aluminum foil.

6. Take another dark measurement.
measured to be about $1.2 \times 10^5 \text{ cm}^{-1}$, or

$$\frac{1}{\alpha} = 83 \text{ nm for } h\nu = 2.3 \text{ eV}.$$  

Although 83 nm is not negligible compared to 133 nm, most of the light actually getting through the blue filter has a penetration depth smaller than this. We thus have a useful tool for probing the surface photoconductance of the films. Comparing the photoconductance with the blue light incident alternately from the front and back sides of the films (see Figure 7.5) should therefore give some indication of the hydrogen concentration profile.

Let photoresponse be defined as the difference between photoconductance and dark conductance. We can then define white response ($\Delta S_W$), front blue response ($\Delta S_F$), and back blue response ($\Delta S_B$) analogously to the respective conductances defined above.

Since as-deposited samples show no white response at room temperature (see Figure 8.4, page 116), they will certainly show no blue response. Let us make the simplest assumption that blue response at room temperature is proportional to the concentration of hydrogen near the surface being probed. Note here that it is instructive to deal with conductances, not conductivities, since the blue response channel will have the same depth (the blue light penetration depth) regardless of the thickness of the sample being measured.

Our ability to compare front blue response and back blue response directly to get a numerical value of the diffusion constant
(D) is limited by the fact that we left the hydrogen plasma on during cooldown.\(^1\) There is thus likely to be more hydrogen on the front surface with respect to the bulk than would be predicted by a complementary error function profile. Furthermore, less light is reflected from the back surface (hence, more is absorbed) than the front owing to the graded index of vacuum/substrate/film as opposed to the more abrupt vacuum/film seen from the front. The ratio of back to front absorptance can be calculated from front and back reflectance measurements for photon energies in the pass band of the blue filter. The result is that 1.26±0.03 times more light is absorbed from the back than the front. This value agrees with front and back blue measurements performed on as-deposited samples at low temperatures. Even though the front blue response cannot be compared directly to the back to obtain D, the 1.26 normalizing factor will be used so that the two hydrogen concentrations may be compared more accurately.

The diffusion constant will be obtained as follows. Let

\[ \rho(x) = \text{concentration of hydrogen at a film depth } x. \quad (12) \]

We assume that

\[ \rho(x) \propto \text{erfc}[x(4Dt)^{-1/2}] \quad \text{for } x > x_0, \quad (13) \]

\(^1\) See Chapter 3 for a discussion of the diffusion of hydrogen into a-Si.
where $t$ is the hydrogenation time and $x_0$ is the depth of the non-erfc fitting front surface layer. Under the assumption that blue response is proportional to hydrogen concentration, we have

$$\Delta S_B(t) = \rho(t).$$  \hspace{1cm} (14)

Measuring two films of thicknesses $\tau_1$ and $\tau_2$ such that $\tau_1, \tau_2 > x_0$, we then have

$$\frac{\Delta S_B(\tau_1)}{\Delta S_B(\tau_2)} = \frac{\rho(\tau_1)}{\rho(\tau_2)} = \frac{\text{erfc}\left[\frac{\tau_1(4Dt)^{-1/2}}{2}\right]}{\text{erfc}\left[\frac{\tau_2(4Dt)^{-1/2}}{2}\right]}.$$  \hspace{1cm} (15)

Because the hydrogen concentration profile and the light attenuation profile result in a photoresponse channel that is the same for all samples hydrogenated at a given temperature (same hydrogenation run) and independent of sample thickness, the front blue response should not vary with $\tau$. Experimentally, of course, this is not the case, and random, albeit in most cases small, fluctuations occur. We expect these fluctuations to be present on the back surface as well, moving in unison with the front surface fluctuations. We can thus

---

1. Recall from Chapter 3 the results of Sol and coworkers (1980) and Dieumegard and coworkers (1979) that for hydrogenation at 400 C, $x_0 = 50$ nm, whereas for 500 C, $x_0 = 200$ nm.
modify equation (15) in a way that makes no difference theoretically but should result in greater experimental accuracy:

\[
\frac{\Delta S_B(\tau_1)/\Delta S_F(\tau_1)}{\Delta S_B(\tau_2)/\Delta S_F(\tau_2)} = \frac{\text{erfc}\left[\tau_1(4Dt)^{-1/2}\right]}{\text{erfc}\left[\tau_2(4Dt)^{-1/2}\right]}.
\] (16)

This equation may be solved numerically for D.
CHAPTER 8

RESULTS

The goal of this study was to investigate the effects of post-deposition hydrogenation on the optical and electrical properties of a-Si thin films prepared by CVD. Emphasis has been placed on the hydrogen concentration profile that results when hydrogen is diffused into the material.

To investigate this profile, we measured the reflectance and transmittance as well as the dc conductance under varying conditions of films having differing thicknesses. We also studied two different hydrogenation temperatures ($T_H = 400$ C and $500$ C) under the assumption that a higher hydrogenation temperature would result in a flatter concentration profile; in this manner, the effects of hydrogen concentration may be distinguished from other effects that may result from varying thickness or from the fact that the front surface of the film is interfaced with air or vacuum while the back surface is interfaced with sapphire.

The instruments, procedures, and mathematical formulas used in this study were described in the preceding chapters. In this chapter the experimental results are presented. The results of the conductance measurements are presented first since they are the most pronounced. Although they clearly identify the concentration profile, conductance measurements cannot reveal how much total hydrogen is
actually incorporated. For this we must turn to the optical measurements, which will be presented subsequently.

Note on Symbols Used in the Figures

Except in certain "typical" curves, where specifically indicated otherwise, the various hexagons, triangles, and squares are used in the figures in this chapter as curve labels, and indicate neither the locations nor the number of data points.

Conductance Measurements

For the purposes of the present work, conductance was found to be a more informative quantity to study than conductivity. Conductivities may, of course, be calculated from the dimensions of the measured region. As described in previous chapters, the samples were 8.8 mm wide with parallel aluminum contacts spaced 0.9 mm apart.

Dark Conductance

Figures 8.1, 8.2, and 8.3 show the dark conductance, $S_{jj}$, as a function of measurement temperature, $T_M$, for films of each nominal thickness (thickness by deposition monitor), 133, 266, and 532 nm, respectively. Each figure contains an as-deposited sample, a sample hydrogenated at 400 C, and a sample hydrogenated at 500 C. Note that in each case there are two regions on the conductance vs. $T_M$ curve, a "high temperature" region ($T_M > 60$ C) where the conductance of the

---

1. Plotted in the figures are log $S_D$ vs. 1000/$T_M$. Inverse temperature is plotted on a linear scale rather than temperature so that the results may be more easily compared to other reports from the Solar Energy Group.
Figure 8.1. Dark Conductance as a Function of Measurement Temperature for Different Hydrogenation Temperatures; Film Thickness = 133 nm.

- As-deposited
- $T_H = 400 \, ^\circC$
- $T_H = 500 \, ^\circC$

See Figure 8.4 for dark conductance data point density.
Figure 8.2. Dark Conductance as a Function of Measurement Temperature for Different Hydrogenation Temperatures; Film Thickness = 266 nm.

- As-deposited
- $T_H = 400$ C
- $T_H = 500$ C

See Figure 8.4 for dark conductance data point density.
Figure 8.3. Dark Conductance as a Function of Measurement Temperature for Different Hydrogenation Temperatures; Film Thickness = 532 nm.

- As-Deposited
- $T_H = 400 \ C$
- $T_H = 500 \ C$

See Figure 8.4 for dark conductance data point density.
hydrogenated samples is greater than that of the as-deposited samples, and a "low temperature" region ($T_H < 60 \, \text{C}$) where the opposite is true. Both effects were previously explained in terms of the reduction of localized gap states with hydrogenation (see Chapter 2, "Electrical Conduction"). The significant points to be made about the dark conductance curves are as follows:

1. There is very little variation in the high temperature conductance ratio (the ratio of the conductance of hydrogenated to that of as-deposited films) with thickness for either $T_H = 400 \, \text{C}$ or $T_H = 500 \, \text{C}$.

2. The high temperature conductance ratio is greater for $T_H = 500 \, \text{C}$ than for $T_H = 400 \, \text{C}$.

3. The low temperature conductance ratio varies greatly with thickness, being smaller (greater hydrogenation effect) for smaller thicknesses.

4. The low temperature conductance ratio is much smaller for $T_H = 500 \, \text{C}$ than for $T_H = 400 \, \text{C}$.

5. The low temperature conductance ratio for the 266 and 532 nm samples hydrogenated at 400 C is comparable to variations observed between different as-deposited samples deposited in the same run.

Points 1, 3, and 4 are easily understood in terms of a parallel resistor model. The hydrogen is assumed to penetrate the silicon film
to a fixed depth, independent of thickness, forming a hydrogen-rich front layer with conductance $S_F$. Beyond that depth resides as-deposited silicon, forming a back layer with conductance $S_B$ that depends on thickness.

At high temperatures, $S_F$ is greater than $S_B$, so most of the current is carried through $S_F$ and we expect little thickness variation in the overall conductance ratio, as is the case. At low temperatures, $S_F$ is much less than $S_B$ and may be considered absolutely nonconducting by comparison, as seen in Figure 8.1 for the thinnest film hydrogenated at 500 °C. The overall conductance will then be dependent only on the thickness of the back layer.

The parallel resistor model is useful to gain a qualitative understanding of the variation of dark conductance with thickness; it is severely limited in its ability to produce quantitative results, as will be shown presently. Let

\[
\begin{align*}
\tau_F &= \text{front layer thickness of the hydrogenated film}, \\
\tau_B &= \text{back layer thickness of the hydrogenated film}, \\
\tau &= \tau_F + \tau_B = \text{total film thickness}, \\
S_{as-dep} &= \text{conductance of the as-deposited film}, \\
S_{hyd} &= \text{conductance of the hydrogenated film}.
\end{align*}
\]

Then according to the parallel resistor model, we should have, at low $T_M$:

If $\frac{S_{\text{hyd}}}{S_{\text{as-dep}}}$ is small (<0.1), it is very likely that there is some hydrogen at the back surface that is reducing the conductance without eliminating it entirely. If $\frac{S_{\text{hyd}}}{S_{\text{as-dep}}}$ is large (>0.3), random fluctuations in samples from the same set could be producing the variation. In either case, an inaccurate value of $\tau_F$ will be obtained.

Notwithstanding these experimental difficulties, $\tau_F$ has been calculated from the data for all three samples hydrogenated at 400 C. Using $-90$ C as a measurement temperature representative of low temperature behavior, results were $\tau_F = 100$, 80, and 180 nm for $\tau = 133$, 266, and 532 nm respectively. Of these, $S_{\text{hyd}}/S_{\text{as-dep}} < 0.3$ holds only for the thinnest sample. For samples hydrogenated at 500 C, only the thickest one has $S_{\text{hyd}}/S_{\text{as-dep}} > 0.1$. Using $T_M = -90$ C as before, we get $\tau_F = 450$ nm for $T_H = 500$ C.

White Response

White conductance is orders of magnitude larger than dark conductance for hydrogenated samples measured at temperatures lower than $-20$ C. As the measurement temperature rises above $-20$ C, the two conductances approach each other as the thermally generated carriers become more numerous, making a significant contribution to the total number of carriers. For as-deposited samples, no white response is seen at all above $-20$ C. Comparisons of the white conductivities of as-deposited samples and samples hydrogenated under various conditions
have previously been made (Schay, 1981; see Figures 3.6 and 3.8 in this thesis). For completeness, Figure 8.4 is presented, showing the dark and white conductances of two films of the same thickness (266 nm), one as-deposited and the other hydrogenated at 500 C. Figure 8.5 shows the white response, $\Delta S_w$, for every hydrogenated sample. Significant observations (at the representative measurement temperature of -105 C) to be made are:

6. For $T_H = 400$ C, the white response for $t = 266$ nm exceeds that for 133 nm by a factor of 2, consistent with uniform conductivity as a function of depth into the film. However, increasing the thickness beyond 266 nm does not increase the response, as demonstrated by the 532 nm film.

7. For $T_H = 500$ C, the white response for $t = 266$ nm exceeds that for 133 nm by a factor of 3, whereas the response for 532 nm exceeds that for 266 nm by a factor of 2.

8. Each film hydrogenated at 400 C has a greater white response than the film of the same thickness hydrogenated at 500 C.

Blue Response

Table 8.1 lists the hydrogenation temperature, $T_H$; the thickness, $t$; the front blue response, $\Delta S_F$; the back blue response, $\Delta S_B$; and the blue response ratio, $\Delta S_B/1.26\Delta S_F$, for each hydrogenated sample. The factor of 1.26, used in the blue response ratio, compensates for
Figure 8.4. Dark and White Conductance as a Function of Measurement Temperature; Film Thickness = 266 nm.

Dark conductance:  ● As-deposited
                 ■ Hydrogenated at 500 C

White conductance:  ○ As-deposited
                   □ Hydrogenated at 500 C

Dots show actual data.
Figure 8.5. White Response as a Function of Measurement Temperature for All Hydrogenated Films.

- $\tau = 133$ nm:  
  - $T_H = 400$ C
  - $T_H = 500$ C

- $\tau = 266$ nm:  
  - $T_H = 400$ C
  - $T_H = 500$ C

- $\tau = 532$ nm:  
  - $T_H = 400$ C
  - $T_H = 500$ C

See Figure 8.4 for white and dark conductance data point density.
Table 8.1. Blue Response

<table>
<thead>
<tr>
<th>$T_H$ (°C)</th>
<th>$\tau$ (nm)</th>
<th>$\Delta S_F$ ($10^{-11} \ \Omega^{-1}$)</th>
<th>$\Delta S_B$ ($10^{-11} \ \Omega^{-1}$)</th>
<th>$\Delta S_B$ 1.26$\Delta S_F$</th>
</tr>
</thead>
<tbody>
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<td>400</td>
<td>133</td>
<td>31.3</td>
<td>8.66</td>
<td>.219</td>
</tr>
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<td>266</td>
<td>53.3</td>
<td>16.1</td>
<td>6.20</td>
<td>.0923</td>
</tr>
<tr>
<td>532</td>
<td>41.3</td>
<td>2.37</td>
<td></td>
<td>.0456</td>
</tr>
<tr>
<td>500</td>
<td>133</td>
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<td>1.71</td>
<td>.334</td>
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<tr>
<td>532</td>
<td>33.3</td>
<td>3.79</td>
<td></td>
<td>.0904</td>
</tr>
</tbody>
</table>
the smaller front absorptance as discussed in Chapter 7. Back blue responses are plotted for each $T_H$ in Figure 8.6. Significant observations to be made are:

9. When films of the same thickness (deposited in the same run) are compared, those hydrogenated at 400 C have a greater back blue response out to 266 nm than those hydrogenated at 500 C.

10. The 532 nm sample hydrogenated at 500 C appears to have anomalously high blue responses. As discussed in Chapter 7, its front blue response should be the same as that of the other samples hydrogenated at 500 C. If we accept that its back blue response should be no greater than that of the 266 nm sample hydrogenated at the same temperature, then point 9 holds out to 532 nm, since even the 532 nm sample hydrogenated at 400 C has a greater back blue response than the 266 nm sample hydrogenated at 500 C.

Optical Measurements

Since optical measurements were performed on the same samples both before (as-deposited) and after hydrogenation, it is advantageous to name the samples so as to be able to distinguish as-deposited

---

1. The sample was remeasured after being cleaned with acetone and alcohol and being soaked in HF. The remeasured blue responses were anomalously low. However, the remeasured blue response ratio was 0.0666, respectably close to the value given in Table 8.1.
Figure 8.6. Back Blue Response as a Function of Sample Thickness for Different Hydrogenation Temperatures.

- $T_H = 400$ C
- $T_H = 500$ C

Symbols show actual data.
samples of the same nominal thickness that are to be hydrogenated at different temperatures. Therefore a two-digit name, n.m, is proposed, wherein n = 1, 2, or 4 is the nominal thickness of the sample in units of 133 nm and m = 4 or 5 is the hydrogenation temperature (either hydrogenated at m or to be hydrogenated at m) in units of 100°C. When necessary, the condition of the sample at the time of the measurement under discussion is denoted by adding -A or -H to indicate "as-deposited" or "hydrogenated" respectively. For example, sample 2.4 has a nominal thickness of 266 nm and either has been or will be hydrogenated at 400°C; sample 4.5-A has a nominal thickness of 532 nm, is as-deposited, and is to be hydrogenated at 500°C.

Infrared Transmittance and Thickness

The primary use of the IR transmittance data was to derive thickness as described in Chapter 6. It is therefore most instructive to plot the IR data as a function of wavelength. The data are shown in Figures 8.7 through 8.12. Each figure displays the data for a single sample before and after hydrogenation.

It was stated previously that the thickness of the thinnest samples could not be measured by IR transmittance since no minima were observed. Figures 8.7 and 8.8 do show a minimum for samples 1.4 and 1.5 around 1900 nm. It is, however, too broad for any meaningful thickness to be derived.

Table 8.2 lists the IR transmittance minima below 1600 nm of samples from the two thicker series, both before and after hydrogenation, the index of the sapphire substrate (after Wolfe, 1978, p. 7-101),
samples of the same nominal thickness that are to be hydrogenated at different temperatures. Therefore a two-digit name, n.m, is proposed, wherein \( n = 1, 2, \) or \( 4 \) is the nominal thickness of the sample in units of 133 nm and \( m = 4 \) or \( 5 \) is the hydrogenation temperature (either hydrogenated at \( m \) or to be hydrogenated at \( m \)) in units of 100 C. When necessary, the condition of the sample at the time of the measurement under discussion is denoted by adding -A or -H to indicate "as-deposited" or "hydrogenated" respectively. For example, sample 2.4 has a nominal thickness of 266 nm and either has been or will be hydrogenated at 400 C; sample 4.5-A has a nominal thickness of 532 nm, is as-deposited, and is to be hydrogenated at 500 C.

Infrared Transmittance and Thickness

The primary use of the IR transmittance data was to derive thickness as described in Chapter 6. It is therefore most instructive to plot the IR data as a function of wavelength. The data are shown in Figures 8.7 through 8.12. Each figure displays the data for a single sample before and after hydrogenation.

It was stated previously that the thickness of the thinnest samples could not be measured by IR transmittance since no minima were observed. Figures 8.7 and 8.8 do show a minimum for samples 1.4 and 1.5 around 1900 nm. It is, however, too broad for any meaningful thickness to be derived.

Table 8.2 lists the IR transmittance minima below 1600 nm of samples from the two thicker series, both before and after hydrogenation, the index of the sapphire substrate (after Wolfe, 1978, p. 7-101),
Figure 8.7. IR Transmittance as a Function of Wavelength for Sample 1.4.

- As-deposited
- Hydrogenated at 400 C

Symbols show actual data.
Figure 8.8. IR Transmittance as a Function of Wavelength for Sample 1.5.

- As-deposited
- Hydrogenated at 500 C

See Figure 8.7 for IR transmittance data point density.
Figure 8.9. IR Transmittance as a Function of Wavelength for Sample 2.4.

- As-deposited
- Hydrogenated at 400 C

See Figure 8.7 for IR transmittance data point density.
Figure 8.10. IR Transmittance as a Function of Wavelength for Sample 2.5.

- As-deposited
- Hydrogenated at 500 C

See Figure 8.7 for IR transmittance data point density.
Figure 8.11. IR Transmittance as a Function of Wavelength for Sample 4.4.

- As-deposited
- Hydrogenated at 400 C

See Figure 8.7 for IR transmittance data point density.
Figure 8.12. IR Transmittance as a Function of Wavelength for Sample 4.5.

- As-deposited
- Hydrogenated at 500 C

See Figure 8.7 for IR transmittance data point density.
Table 8.2. IR Transmittance Minima and Film Thicknesses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavelength (nm)</th>
<th>Transmittance</th>
<th>Substrate index</th>
<th>Film index</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4-A</td>
<td>1290</td>
<td>.392</td>
<td>1.751</td>
<td>3.685</td>
<td>263</td>
</tr>
<tr>
<td>2.4-H</td>
<td>1280</td>
<td>.402</td>
<td>1.751</td>
<td>3.623</td>
<td>265</td>
</tr>
<tr>
<td>4.4-A</td>
<td>1105</td>
<td>.395</td>
<td>1.754</td>
<td>3.668</td>
<td>527</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>.410</td>
<td>1.747</td>
<td>3.571</td>
<td>525</td>
</tr>
<tr>
<td>4.4-H</td>
<td>1100</td>
<td>.403</td>
<td>1.754</td>
<td>3.619</td>
<td>532</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>.414</td>
<td>1.747</td>
<td>3.548</td>
<td>529</td>
</tr>
<tr>
<td>2.5-A</td>
<td>1270</td>
<td>.390</td>
<td>1.751</td>
<td>3.697</td>
<td>258</td>
</tr>
<tr>
<td>2.5-H</td>
<td>1255</td>
<td>.398</td>
<td>1.751</td>
<td>3.647</td>
<td>258</td>
</tr>
<tr>
<td>4.5-A</td>
<td>1015</td>
<td>.397</td>
<td>1.756</td>
<td>3.657</td>
<td>485</td>
</tr>
<tr>
<td></td>
<td>1370</td>
<td>.413</td>
<td>1.749</td>
<td>3.555</td>
<td>481</td>
</tr>
<tr>
<td>4.5-H</td>
<td>1010</td>
<td>.404</td>
<td>1.756</td>
<td>3.627</td>
<td>487</td>
</tr>
<tr>
<td></td>
<td>1365</td>
<td>.414</td>
<td>1.749</td>
<td>3.550</td>
<td>481</td>
</tr>
</tbody>
</table>
and the derived film index and thickness according to equations (7) and (8) of Chapter 6.

Visible Absorption

Figures 8.13 through 8.18 show the reflectance and transmittance of each sample before and after hydrogenation for photon energies from 1.4 to 2.4 eV. From these figures, it appears as though a greater effect is seen in samples hydrogenated at 400 C rather than 500 C. This appearance is deceptive, however, as we shall see shortly.

The internal absorptance of thin films cannot be determined (unless it is zero) without calculating the optical constants. However, the quantity \( \frac{1-T-R}{1-R} \) should give an indication of the internal absorptance and has the advantage of being a directly measurable quantity. Figures 8.19 and 8.20 show \( \frac{1-T-R}{1-R} \) as a function of photon energy for all samples in this study. These plots clearly show a greater effect in samples hydrogenated at 500 C in the higher photon energy (>1.7 eV) range. In the lower photon energy range, a greater effect is seen in the samples hydrogenated at 400 C. However, contrary to expectations (see Chapter 2, "Optical Properties"), hydrogenation at 400 C increases the "internal absorptance" for low photon energy. Hydrogenation at 500 C, on the other hand, decreases "internal absorptance" throughout the measurable range.

The interpretation of the larger reflectance effect seen at 400 C is straightforward. Samples hydrogenated at 400 C have a larger concentration of hydrogen on their front surface. Since reflection
Figure 8.13. Visible Transmittance and Reflectance as a Function of Photon Energy for Sample 1.4.

Transmittance: ○ As-deposited
△ Hydrogenated at 400 C

Reflectance: ■ As-deposited
▲ Hydrogenated at 400 C

Dots show actual data.
Figure 8.14. Visible Transmittance and Reflectance as a Function of Photon Energy for Sample 1.5.

Transmittance: ○ As-deposited
□ Hydrogenated at 500 C

Reflectance: ● As-deposited
■ Hydrogenated at 500 C

See Figure 8.13 for transmittance and reflectance data point density.
Figure 8.15. Visible Transmittance and Reflectance as a Function of Photon Energy for Sample 2.4.

Transmittance:  ○ As-deposited  △ Hydrogenated at 400 C

Reflectance:  ● As-deposited  ▲ Hydrogenated at 400 C

See Figure 8.13 for transmittance and reflectance data point density.
Figure 8.16. Visible Transmittance and Reflectance as a Function of Photon Energy for Sample 2.5.

Transmittance:  ○ As-deposited
                 □ Hydrogenated at 500 C

Reflectance:    ◇ As-deposited
                 □ Hydrogenated at 500 C

See Figure 8.13 for transmittance and reflectance data point density.
Figure 8.17. Visible Transmittance and Reflectance as a Function of Photon Energy for Sample 4,4.

Transmittance:  
- ○ As-deposited  
- Δ Hydrogenated at 400 C  

Reflectance:  
- ● As-deposited  
- ▲ Hydrogenated at 400 C  

See Figure 8.13 for transmittance and reflectance data point density.
Figure 8.18. Visible Transmittance and Reflectance as a Function of Photon Energy for Sample 4.5.

Transmittance:  
- As-deposited
- Hydrogenated at 500 C

Reflectance:  
- As-deposited
- Hydrogenated at 500 C

See Figure 8.13 for transmittance and reflectance data point density.
Figure 8.19. $\frac{1-T-R}{1-R}$ as a Function of Photon Energy for Films of Different Thicknesses, As-Deposited and Hydrogenated at 400 C.

Sample 1.4:  
• As-deposited  
○ Hydrogenated at 400 C

Sample 2.4:  
▲ As-deposited  
△ Hydrogenated at 400 C

Sample 4.4:  
■ As-deposited  
□ Hydrogenated at 400 C

See Figure 8.13 for transmittance and reflectance data point density.
Figure 8.20. $\frac{1-T-R}{1-R}$ as a Function of Photon Energy for Films of Different Thicknesses, As-Deposited and Hydrogenated at 500 C.

Sample 1.5:  
- As-deposited
- Hydrogenated at 500 C

Sample 2.5:  
- As-deposited
- Hydrogenated at 500 C

Sample 4.5:  
- As-deposited
- Hydrogenated at 500 C

See Figure 8.13 for transmittance and reflectance data point density.
from the front surface is the major component of reflection for absorbing films, a greater effect should be seen when more hydrogen resides near the front surface. Furthermore, a smaller front surface reflection (the effect of hydrogenation) results in more light initially getting into the film. It would thus not be surprising if a greater transmittance shift were seen in samples hydrogenated at 400 C even though the overall shift in $\alpha$ was smaller. We note, however, that the transmittance shift for $T_H = 500$ C is at least as large as for $T_H = 400$ C.

The optical constants, $n$ and $k$, were derived from the reflectance and transmittance measurements according to the method discussed in Chapter 6. Figures 8.21 through 8.26 are plots of $(\alpha \nu)^{1/2}$ vs. the photon energy $\nu$, where $\alpha = 4\pi k/\lambda$ is the absorption coefficient. The same trends are seen as with $\frac{1-T-R}{1-k}$: Hydrogenation at 500 C produces a larger shift than at 400 C, and hydrogenation at 400 C increases $\alpha$ in the low photon energy range.

The $(\alpha \nu)^{1/2}$ vs. $\nu$ data for samples 1.5, 2.5, and 4.5 were analyzed by linear regression for $(\alpha \nu)^{1/2} > 120$ (eV/cm)$^{1/2}$. The extrapolations of the resulting lines to $(\alpha \nu)^{1/2} = 0$ for samples 1.5 and 2.5 are shown in Figures 8.22 and 8.24 respectively. The as-deposited and hydrogenated lines for sample 4.5 are too close together on the scale of Figure 8.26 to make their inclusion meaningful. Although not readily apparent from the figures, $(\alpha \nu)^{1/2}$ vs. $\nu$ has in each case a small but positive second derivative above 1.7 eV. This observation is not without precedent (Fritzsche, 1980).
Figure 8.21. \((\text{ahv})^{1/2}\) as a Function of Photon Energy for Sample 1.4.

- As-deposited
- Hydrogenated at 400 C

See Figure 8.22 for \((\text{ahv})^{1/2}\) data point density.
Figure 8.22. $(\alpha h\nu)^{1/2}$ as a Function of Photon Energy for Sample 1.5.

- As-deposited
- Hydrogenated at 500 C

--- Extrapolation of linear fit for $(\alpha h\nu)^{1/2} > 120 \text{ (eV/cm)}^{1/2}$

Dots show actual data.
Figure 8.23. \((ahv)^{1/2}\) as a Function of Photon Energy for Sample 2.4.

- As-deposited
- Hydrogenated at 400 C

See Figure 8.22 for \((ahv)^{1/2}\) data point density.
Figure 8.24. \((\alpha h \nu)^{1/2}\) as a Function of Photon Energy for Sample 2.5.

- As-deposited
- Hydrogenated at 500 C

--- Extrapolation of linear fit for \((\alpha h \nu)^{1/2} > 120 \ (eV/cm)^{1/2}\)

See Figure 8.22 for \((\alpha h \nu)^{1/2}\) data point density.
Figure 8.25. $(\alpha h\nu)^{1/2}$ as a Function of Photon Energy for Sample 4.4.

- As-deposited
- Hydrogenated at 400 C

See Figure 8.22 for $(\alpha h\nu)^{1/2}$ data point density.
Figure 8.26. \((\alpha h\nu)^{1/2}\) as a Function of Photon Energy for Sample 4.5.

- As-deposited
- Hydrogenated at 500 C

See Figure 8.22 for \((\alpha h\nu)^{1/2}\) data point density.
Index of Refraction

The index of refraction, \( n \), was computed for all films at all wavelengths measured as described in Chapter 6. The data are mostly scattered, however, and little can be said about the change in \( n \) with hydrogenation except that it tends to be reduced. The computed index for hydrogenated films is lower by differing amounts in different parts of the spectrum such that no pair of continuous curves may be drawn through the data to indicate the overall effect of hydrogenation.

The problems associated with the computation of \( n \) are attributed mainly to errors in the thickness determination; the data were most consistent for the thickest films, which had two sharp IR transmittance minima from which to derive thickness. For these samples, of course, the effect of hydrogenation was smallest. For completeness, the index of refraction computed for sample 4.5-A is shown in Figure 8.27.
Figure 8.27. Index of Refraction as a Function of Photon Energy for Sample 4.5-A.

Dots show actual data.
CHAPTER 9

DISCUSSION

To explain the results presented in the previous chapter, we must understand both the effect of hydrogen on the properties of amorphous silicon and the hydrogen concentration profile within the material. The current understanding of the properties of a-Si and of the effect of hydrogen on these properties was explained in Chapters 1 and 2. Chapter 1 dealt briefly with the density of localized (electron) states in a-Si; states resulting both from the amorphous nature of the material and from defects were discussed. Chapter 2 discussed how these states affect measurable properties of amorphous silicon, namely, its conductivity and optical constants, and how hydrogen may be employed to neutralize the localized states. It will be shown in this chapter, however, that the current understanding of the effect of hydrogen is inadequate to explain all the results of Chapter 8, regardless of the concentration profile hypothesized.

Old Model

We describe the action of hydrogen on a-Si as follows:

Hydrogen either has no effect or--

a. increases the extended carrier path length and

b. reduces the number and/or mobility of localized carriers.
We suppose that the primary mechanism for the effect of hydrogen is the termination of dangling bonds. Also included in the above model, however, is the possibility that H breaks an Si-Si bond and attaches to the resulting dangling bonds: If the original Si-Si bond is strained enough, H will probably have the same effect as it has when it terminates a lone dangling bond; if the Si-Si bond is not very strained, H may have no effect. Interstitial hydrogen is assumed to have no effect.

The relative profiles of effective (bonded) hydrogen may be deduced from the blue measurements alone (see Table 8.1 and Figure 8.6). As discussed in Chapter 8, the back blue response can be presumed to be greater for hydrogenation at 400 C than at 500 C for all sample thicknesses. Therefore, according to the present model, there must be more effective hydrogen at all depths in films hydrogenated at 400 C than in those hydrogenated at 500 C. Figure 9.1 shows how the effective hydrogen concentration profiles for each hydrogenation might look. The profiles are in agreement with the white measurements, which show a greater white response for samples hydrogenated at 400 C for all sample thicknesses.

The profiles of Figure 9.1 cannot be used to explain the dark measurements, however, which were shown in Figures 8.1 through 8.3. A greater effect at low measurement temperature is clearly seen for samples hydrogenated at 500 C, indicating that more effective hydrogen reaches the back surface for these samples.
Figure 9.1. Hydrogen Concentration Profiles Demanded by the Blue Measurements Under the Old Model.
New Model

We propose that hydrogen exists in the silicon lattice in two forms with the following effects:

Hydrogen bonded to silicon (same effect as in the old model)—

1a. increases the extended carrier path length and
1b. reduces the number and/or mobility of localized carriers.

Interstitial hydrogen—

2a. contributes to photoconductivity by increasing the number of photogenerated carriers and
2b. reduces the extended carrier path length, but to a lesser extent than bonded hydrogen increases it—optional.

The properties of bonded hydrogen are those of the old model and are explained in Chapter 2. Interstitial effects are explained by supposing that—

3a. the electron on an interstitial hydrogen is much more likely to be excited to the conduction band (by incident light)—and become free of the resulting hole—than an extended electron in the valence band, and
3b. interstitial hydrogen scatters extended carriers—optional.

All the electrical properties may be explained if we suppose that the profiles of bonded and interstitial hydrogen are given by Figure 9.2.
Figure 9.2. Proposed Hydrogen Concentration Profiles Under the New Model.
Basically, bonded hydrogen explains the dark conductance effects and interstitial hydrogen explains the photoconductance effects. However, effect 2b explains why the high temperature dark conductance is smaller for \( T_H = 400 \) C than for \( T_H = 500 \) C (see Figures 8.1 through 8.3). Effect 2b is necessary only if we suppose that the concentration of bonded hydrogen is greater near the surface of the 400 C hydrogenated films.

This model is not contradicted by theoretical calculations, which show that the energy level of the electron on an interstitial hydrogen is near the valence band edge in c-Si (Singh et al., 1977; Rodriguez, Jaros, and Brand, 1979). The proximity to the band edge explains the absence of experimental evidence for the energy of this state.

The new model has difficulty explaining the optical measurements, which show very little effect of hydrogenation by comparison to the order-of-magnitude effects seen in conductance. If we suppose that all absorption in the visible region is due to carrier excitation, then a factor of 10 increase in the absorptance from hydrogenation at 500 C to hydrogenation at 400 C is predicted by the photoconductance (see especially the white conductance) measurements under the present model. The excess photoconductance for \( T_H = 400 \) C cannot be the result of increased carrier mobility (according to the dark measurements) unless we presume that the primary mechanism for photoconductance is hopping. The latter assumption is contradicted by the fact that the photoconductance after hydrogenation is much greater than before, for all measurement temperatures.
The optical measurements are in agreement, however, if we assume that extended electrons in the valence band are just as likely to be excited by incident light as the electron on an interstitial hydrogen atom, with the caveat that in the former case the electron and hole created undergo geminate recombination. What prevents geminate recombination in the case of the interstitial hydrogen is not understood.

The small optical bandgap shift observed in hydrogenated samples cannot be an effect of interstitial hydrogen since it is smaller in samples hydrogenated at 400 C. We therefore conclude that it is an effect of bonded hydrogen and attribute it to the greater bond energy of Si-H over Si-Si. The greater shifts in samples hydrogenated at 500 C thus indicate a greater quantity of bonded hydrogen in these samples.

Diffusion Constant

It is far more likely for a hydrogen to jump from one interstitial site to another than for a hydrogen to leave a bonding site and become interstitial.\(^1\) To measure the diffusion constant, therefore, we must measure the concentration of interstitial hydrogen. Fortunately, the photoresponse is an interstitial effect under the new model, so equation (16) of Chapter 7 may be used to measure D.

---

\(^1\) There are too few dangling bonds in the as-deposited material (see Figure 2.2) to consider hydrogen jumping from one bonding site to another as a diffusion mechanism.
Diffusion constants were calculated from the blue response ratios of Table 8.1 using films from the two thicker series only, because it may be that the complementary error function profile does not hold as near to the front surface as 133 nm (see Chapter 7). The results are

\[ D = 7.2 \times 10^{-13} \, \text{cm}^2/\text{sec for } T_H = 400 \, \text{C} \]

and

\[ D = 3.4 \times 10^{-12} \, \text{cm}^2/\text{sec for } T_H = 500 \, \text{C}. \]

The result for 500 C is in close agreement with the results of Dieumegard and coworkers (1979). For 400 C, on the other hand, the value measured here is 12 times greater than that reported by Sol and coworkers (1980). Ironically, it is the result for \( T_H = 500 \, \text{C} \) that is most doubtful considering the large difference between the front blue response of the thickest film and that of the other two also hydrogenated at 500 C.\(^1\)

Total Concentration of Bonded Hydrogen

Fritzsche (1980) has compiled optical bandgap, \( E_0 \), vs. at.\% H data for a-Si films deposited by PVD, GD, and CVD. The data are shown here as Figure 9.3. Although they are quite scattered, a straight line fit is not unreasonable and is shown on the figure. Assuming that our as-deposited films have no incorporated hydrogen on the scale of Figure 9.3 (see Figure 3.2), only the bandgap of sample 4.5-A falls on

---

1. The front blue response of all samples hydrogenated at the same temperature should be the same regardless of thickness (see Chapter 7). However, when the thickest sample was remeasured, its blue responses were lower by a factor of 30, while the blue response ratio changed by only 26%.
Figure 9.3. Optical Bandgap as a Function of Hydrogen Concentration in a-Si.

After Fritzsche (1980).
the line, while 2.5-A and 1.5-A lie somewhat above it. Even so, it is not unreasonable to suppose that hydrogenation produces a change in $E_0$, which is given by the slope of the linear fit in Figure 9.3, 0.0147 eV, times the at.% of bonded hydrogen. Table 9.1 lists the optical bandgaps of the films analyzed by linear regression before and after hydrogenation, together with the change in bandgap, $\Delta E_0$, and the at.% bonded H added by hydrogenation as computed from at.% bonded H = $\Delta E_0/(0.0147 \text{ eV})$.

It is clear that very little bonded hydrogen is being added to the films by hydrogenation in our reactor. This is to be expected since the atomic density of CVD a-Si is about $5\times10^{22} \text{ cm}^{-3}$, while the spin density of the as-deposited material is about $10^{19} \text{ cm}^{-3}$ (see Figure 2.2). It would thus take only 0.02 at.% bonded hydrogen to terminate all of them. The fact that we measured larger concentrations might be attributed to experimental error (the difference, although orders of magnitude, is very small on an absolute scale). However, the regularity of the optical measurements suggests a different explanation.

As explained in Chapter 2, strained Si-Si bonds have no unpaired spins, yet can be broken by hydrogen, resulting in either an Si-H bond and a dangling bond or two Si-H bonds. Since strained Si-Si electronic states can be found inside the bandgap, the effect on conductance can be the same as if hydrogen had terminated a dangling bond. Furthermore, since the hydrogen is bonded to silicon, it would be expected to increase the bandgap as well.
Table 9.1. Optical Bandgaps Before and After Hydrogenation at 500 C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_0$ as-deposited (eV)</th>
<th>$E_0$ hydrogenated (eV)</th>
<th>$\Delta E_0$ (eV)</th>
<th>At.% hydrogen added by hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>1.5904</td>
<td>1.6116</td>
<td>0.0212</td>
<td>1.44</td>
</tr>
<tr>
<td>2.5</td>
<td>1.5233</td>
<td>1.5327</td>
<td>0.0094</td>
<td>0.64</td>
</tr>
<tr>
<td>4.5</td>
<td>1.5034</td>
<td>1.5116</td>
<td>0.0082</td>
<td>0.56</td>
</tr>
</tbody>
</table>
We must also consider the possibility that hydrogen might break an unstrained Si-Si bond. If both resulting dangling bonds are subsequently terminated by hydrogen, the effect on conductance will be negligible but the bandgap would be increased. The probability of hydrogen breaking an unstrained bond is clearly small; otherwise, there would be no interstitial hydrogen.

The model proposed here is clearly speculative, but it does provide a fairly simple picture on the basis of which all the data may be explained. Although there is not a large body of data to support this model, it is clear that the simple assumption that interstitial hydrogen is totally inert in the a-Si:H system must be examined further.
SUMMARY AND CONCLUSIONS

Starting from a general discussion of photovoltaic solar energy conversion, I have explained the advantages of thin film silicon as a material for such systems. Thin films as produced, however, are usually amorphous or polycrystalline and have structural defects that reduce the electron and hole diffusion lengths and thus the efficiency of the cell. I then discussed how these defects affect the conductivity, making them accessible to simple measurements. I pointed out that CVD prepared films are grown in thermal equilibrium, which results in a densely packed amorphous material, thought to be free of most defects except for dangling bonds. I then explained how hydrogen may be used to terminate these dangling bonds, reducing their effect on the conductivity. The effect of incorporated hydrogen on the optical properties of a-Si was discussed as another tool for detecting its presence.

Since most of the hydrogen present in the silane molecule is released during chemical vapor deposition, it must be reintroduced by diffusion after deposition. Several previous reports from the photovoltaic group at the Optical Sciences Center have examined the effects of post-deposition hydrogenation on the electrical and photovoltaic properties of CVD a-Si (Schay, 1981; Strobl, 1981; Köberle, 1982; Hey and
Seraphin, 1982). In particular, they have shown that post-deposition hydrogenation can greatly reduce hopping conductance (low temperature dark conductance) and improve photoresponse.

In this thesis, problems associated with the inhomogeneous hydrogen concentration profile, which results from the diffusion process, were examined by analyzing samples of various thicknesses hydrogenated at two different temperatures. The procedures, instruments, and mathematical formulas used in this venture were presented in Chapters 4 through 7.

The results of this study were presented in Chapter 8 and discussed in Chapter 9. As expected, hydrogenation at 400 C resulted in a greater hydrogen surface concentration and a smaller diffusion constant than hydrogenation at 500 C. Although the overall density of bonded hydrogen in films hydrogenated at 500 C appears to be greater than the original dangling bond density, most of it resides near the front surface; hopping conduction is eliminated only in the first 200 to 300 nm of film depth. Even on the front surface, however, films hydrogenated at 500 C are not saturated with hydrogen with respect to photoresponse.

It was demonstrated in Chapter 9 that the results cannot be explained using current models of the effect of hydrogen on a-Si. A new model was suggested to explain the data. According to the new model, interstitial hydrogen plays a greater role in photoconductance than previously believed, while dark conductance and optical bandgap effects are attributed to bonded hydrogen. It was further suggested
that strained bonds might play a greater role in the properties of as-deposited CVD a-Si than previously thought.

The post-deposition hydrogenation at 500 °C of CVD a-Si results in a material that appears to have few localized states in the first 200 nm of film depth. A photovoltaic device made from this material should therefore have its charge-separating junction within this active depth.
GLOSSARY

Acronyms

AMI  Air mass one
CVD  Chemical vapor deposition
ESR  Electron spin resonance
GD   Glow discharge
IR   Infrared
NIR  Near infrared
PVD  Physical vapor deposition
rf   Radio frequency
UV   Ultraviolet

Symbols

a-Si  Amorphous silicon
c-Si  Crystalline silicon
D     Diffusion constant: The concentration of one material diffused into another at constant temperature attenuates with depth according to $\text{erfc}(x(4Dt)^{-1/2})$, where $t$ is diffusion time and $x$ is depth into the host material.
d_{act}  Active thickness: The active thickness of a solar cell is the lesser of $1/\alpha$ and $1_{\text{diff}}$.
$E_g$  Optical bandgap: An approximation to $E_g$, the optical bandgap is the intercept of the linear portion of the $(\omega \nu)^{1/2}$ vs. $\nu$ curve with the $\nu$ axis.
$E_g$  Extended state bandgap
erfc Complementary error function
$l_{\text{diff}}$ Diffusion length: The diffusion length of a free carrier in a semiconductor is the average distance it travels after excitation and before recombination.

$\log$ Common logarithm

$N_S$ Spin density

$\tilde{n}$ Complex index of refraction: The convention used in this thesis is $\tilde{n} = n - ik$.

$R_{ij}^M$ Measured reflectance (notation applies in Chapter 6 only; see Table 6.2 and Figure 6.3 for subscript meaning)

$T_{ij}^M$ Measured transmittance (notation applies in Chapter 6 only)

$T_D$ Deposition temperature

$T_H$ Hydrogenation temperature

$T_M$ Measurement temperature

$W_p$ Peak watt: A unit used in solar cell cost comparisons; $W_p$ means "per watt at peak power generation".

$\alpha$ Absorption coefficient: The intensity of light attenuates in an absorbing medium according to $\exp(-\alpha x)$, where $x$ is depth into the medium.

**Terms**

Absorption edge: A roughly defined range of wavelengths or photon energies around which a material passes from being transparent to opaque

Blue conductance: See photoconductance

Blue response: See photoresponse

Blue response ratio: The ratio of the back blue response to the front blue response normalized to account for the excess light absorbed from the back

Dark conductance: The conductance of a film under no illumination
Photoconductance: The conductance of a film under illumination. Included as photoconductance are—

Blue conductance: The conductance of a film under blue illumination, as defined by Figure 7.7. Included as blue conductance are—

Front blue conductance: Blue conductance under illumination from the film side of the film/substrate tandem.

Back blue conductance: Blue conductance under illumination from the substrate side of the film/substrate tandem.

White conductance: The conductance of a film under white illumination, as defined by Figure 7.7. All white conductance measurements were taken under illumination from the film side.

Photoresponse: The difference between photoconductance and dark conductance. Blue response (front and back) and white response are defined with respect to blue conductance and white conductance respectively.

Saturated: A material M is saturated with a substance S with respect to an effect E if and only if any further addition of S to M will produce no change in E.

Thick film: A film that shows no interference effects in reflection or transmission.

Thin film: A film that shows interference effects in reflection or transmission. The identity of a film as thick or thin depends on the wavelength of light being observed and the resolving power of the monochromator as well as the thickness and surface roughness of the film.

White conductance: See photoconductance

White response: See photoresponse
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