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AMORPHOUS SILICON SOLAR CELLS

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Improvements in the photoluminescence, the photoconductivity, and the collection efficiency of films after annealing at $\sim 200\text{--}300^\circ\text{C}$ indicate that many defects within the gap are being annealed out of the films at these temperatures.

The conduction behavior in the field regime of $\sim 10^4\text{--}10^5$ V/cm appears to be due to the Poole-Frenkel effect. At lower fields the conduction is ohmic and thermally activated, but the pre-exponential term σ_0 obeys the Meyer-Neldel rule ($\sigma_0 = \sigma_{00} \exp(E_a/kT_0)$).

Recent experiments with lightly doped, p-type a-Si indicate that this amorphous silicon is a good-quality solar cell material.

Pd Schottky-barrier cells without antireflection coatings have shown no degradation after 4400 hours of continuous illumination ($\sim 50\text{--}75$ mW/cm²).

PREFACE

This quarterly report covers the work performed by the Materials Research Laboratory of RCA Laboratories, Princeton, NJ, for the period 1 October 1976 to 31 December 1976 under Contract No. E(04-3)-1286. The Laboratory Director is Paul Rappaport; B. F. Williams is the Group Head, and D. E. Carlson is the Project Scientist.

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SECTION I

INTRODUCTION

The amorphous silicon solar cell [1] was first developed at RCA Laboratories in 1974. This cell utilizes $\sim 1 \mu\text{m}$ of amorphous silicon (a-Si) deposited from a glow discharge in silane (SiH_4). The films are deposited at substrate temperatures of 200–500°C and at deposition rates of 0.1–1.0 $\mu\text{m}/\text{min}$. Most conductive materials can be used as substrates, but steel sheet is preferred due to its low cost.

The best power conversion efficiency obtained to date is 5.5% for a Pt Schottky barrier cell using a ZrO_2 antireflection coating [2]. The theoretical limit for the efficiency of thin-film, a-Si solar cells is estimated to be $\sim 15\%$ [1].

The electrical and optical properties of discharge-produced a-Si are significantly different from those of single-crystal Si. The optical absorption coefficient exceeds that of single-crystal Si by an order of magnitude over most of the visible light range; thus, only $\sim 1 \mu\text{m}$ of a-Si is needed to absorb a considerable fraction of the solar radiation. The optical bandgap of discharge-produced a-Si is ~ 1.6 – 1.8 eV as compared with 1.12 eV for crystalline Si. Pt Schottky-barrier heights of ~ 1.2 eV have been measured on a-Si as compared with 0.8 eV on crystalline Si. A-Si diodes exhibit electroluminescence [3] at $h\nu \sim 1.3$ eV at 77°K, and the intensity is several orders of magnitude greater than that observed in single-crystal Si at $h\nu \sim 1.09$ eV. The recombination lifetime in a-Si is on the order of 10 μs , a value that can be achieved only in high-purity single-crystal Si. Moreover, a-Si Schottky-barrier cells exhibit near-ideal diode behavior in the dark [4].

1. D. E. Carlson and C. R. Wronski, "Amorphous Silicon Solar Cell," Appl. Phys. Letters 28, 671 (1976).
2. D. E. Carlson, C. R. Wronski, A. R. Triano, and R. E. Daniel, "Solar Cells Using Schottky Barriers on Amorphous Silicon," to be published in Proc. 12th Photovoltaic Specialists Conf., Baton Rouge, LA, November 15–18, 1976.
3. J. I. Pankove and D. E. Carlson, "Electroluminescence in Amorphous Silicon," Appl. Phys. Letters 29, 620 (1976).
4. C. R. Wronski, D. E. Carlson, and R. E. Daniel, "Schottky Barrier Characteristics of Metal-Amorphous Silicon Diodes," Appl. Phys. Letters 29, 602 (1976).

SECTION II

TECHNICAL DISCUSSION

A. DEPOSITION SYSTEMS

Since the properties of a-Si produced in a silane (SiH_4) discharge depend strongly on the deposition conditions, four types of deposition systems are being investigated: a dc discharge system with the substrate as a cathode; a dc system with a cathodic screen located near the substrate; an electroless rf system; and a capacitive rf system.

To date, the most conductive doped films have been deposited in the dc discharge by means of a cathodic screen in proximity to the substrate. However, the best-quality undoped films have been produced in the rf discharges. The largest open-circuit voltages ($V_{oc} \approx 865$ mV) have been observed in films produced in an electroless rf discharge. These films have also exhibited the lowest space-charge densities ($\sim 10^{15}/\text{cm}^3$) as determined from capacitance-voltage measurements on diodes. Preliminary data obtained with the capacitive rf system indicate good collection efficiencies. More emphasis will be placed on optimizing the capacitive rf system in the next quarter.

B. SUBSTRATE PREPARATION

Most of the a-Si diodes are presently being fabricated on substrates of steel, stainless steel, Nb, or Ta. Compositional profiles of diodes obtained by Auger electron spectrometry and secondary ion mass spectrometry show that an oxide layer usually exists at the a-Si/substrate interface. This oxide layer can be reduced considerably by heating the substrate to $\sim 400^\circ\text{C}$ and exposing it to a glow discharge in an atmosphere of Ar and H_2 . Cells with series resistance as low as $6\ \Omega\text{-cm}^2$ in the dark and $1.8\ \Omega\text{-cm}^2$ in AM1 sunlight have been prepared by means of this technique.

C. FILM PROPERTIES

1. Hydrogen Content

The hydrogen content of film produced in a SiH_4 discharge has been measured by means of infrared absorption and secondary ion mass spectrometry (SIMS). The infrared absorption spectrum exhibits lines at $\lambda \sim 5$ and $15.8 \mu\text{m}$; the first is believed to be the Si-H stretching mode, and the latter, the Si-H bending mode. The concentration of bonded hydrogen is estimated, based on the published results for the absorption due to the Si-H bending mode [5]. The substrates used were either single-crystal Si or single-crystal Ge for substrate temperatures $T_s \lesssim 300^\circ\text{C}$. For higher values of T_s , $500 \text{ \AA}$ of SiO_2 was deposited on the single-crystal Si and Ge to prevent epitaxy or induced crystallization.

Figure 1 shows the concentration of bonded hydrogen in at. % for a series of a-Si films deposited at various substrate temperatures using both rf(E) electroless and dc(C) cathodic glow discharges. In both cases, the bonded hydrogen content decreases with increasing substrate temperature, but larger concentrations are observed in the films deposited at low substrate temperatures using an rf(E) discharge.

The symmetry properties of the bonding can be examined by comparing the ratios of the absorption of the Si-H stretching and bending modes. The films produced in the dc(C) discharge show a ratio of ~ 0.45 ; this is close to that observed in SiH_4 . However, the films produced in the rf(E) discharge give a ratio of ~ 0.36 , closer to that expected for a lower-symmetry group such as SiD_3H . When films were deposited on single-crystal Si at substrate temperatures $>300^\circ\text{C}$, the films appeared hazy, and the ratio of the stretching-mode to that of the bending-mode absorption decreased considerably. This decrease in the ratio may be related to crystallization effects, since the normal values were obtained if the Si crystal substrate was first covered with $\sim 500 \text{ \AA}$ of SiO_2 .

The film deposited at $\sim 30^\circ\text{C}$ in a dc(C) discharge was also examined by SIMS. A single-crystal Si sample implanted with a known dose of protons was

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5. G. A. N. Connell and J. R. Pawlik, "Use of Hydrogenation in Structural and Electronic Studies of Gap States in Amorphous Germanium," *Phys. Rev. B* **13**, 787 (1976).

Figure 1. Atomic % of bonded hydrogen as a function of substrate temperature.

used to calibrate the spectrometer. The total hydrogen content of the a-Si film was estimated to be ~ 8.5 at. %, a value in good agreement with the estimate of ~ 9.3 at. % for the Si-H concentration from the infrared absorption data. These results indicate that most of the hydrogen is bonded, and that interstitial hydrogen atoms and molecules constitute less than ~ 1 at. % of the a-Si films.

The concentration of bonded hydrogen in the film deposited at $\sim 110^{\circ}\text{C}$ in an rf(E) discharge is ~ 16 at. %; this value agrees well with the determination of ~ 15 at. % for films deposited at approximately room temperature in an rf discharge [6]. In the latter case, the total hydrogen content was determined by measuring the pressure of hydrogen evolved when the films were heated above the crystallization temperature in a glass ampule.

6. A. Triska, D. Dennison, and H. Fritzsche, "Hydrogen Content in Amorphous Ge and Si Prepared by RF Decomposition of GeH_4 and SiH_4 ," Bull. Am. Phys. Soc. 20, 392 (1975).

Preliminary annealing experiments in vacuum indicate that hydrogen evolves from the a-Si films when they are heated above the temperature at which they were deposited. Infrared absorption measurements indicate that the bonded-hydrogen content falls to values expected for films deposited at the annealing temperature; i.e., for a film deposited at 110°C and then annealed at 200°C, the hydrogen content falls from ~16 to ~10.2 at. %, close to the value expected for a film deposited at 200°C.

When a-Si films were made in discharge atmospheres containing 10% SiH₄ and 90% H₂, additional absorption lines appeared in the infrared spectrum. These additional absorption lines were also evident in films deposited at low temperatures, and may correspond to H-Si-H bonds.

Films made in discharge atmospheres containing 10% SiH₄ and 90% D₂ exhibited infrared absorption lines due to both Si-H and Si-D vibrational modes. Since the intensities of these modes were comparable and the D/H ratio in the atmosphere was 4.5:1, it may be concluded that the molecules were not completely dissociated by the discharge.

2. Optical Properties

Earlier work showed the absorption coefficient of discharged-produced a-Si in the visible light range to have increased significantly with increasing substrate temperature [7]. As shown by the data in Fig. 2, the optical gap, ϵ_{OPT} , decreases as the substrate temperature increases. The plots shown in Fig. 2 of $(\alpha h\nu)^{1/2}$ vs $h\nu$ are the same as those used in the analysis of indirect bandgap semiconductors. This relationship can be derived simply by assuming parabolic band edges and matrix elements for the optical transitions that are independent of energy [8].

7. D. E. Carlson, "Amorphous Silicon Solar Cell," Quarterly Report No. 1 prepared for U.S. Energy Research and Development Administration under Contract No. E(04-3)-1286, October 1976.
8. E. A. Davis, "Optical Properties of Amorphous Semiconductors," in P. G. LeComber and J. Mort, eds., *Electronic and Structural Properties of Amorphous Semiconductors* (Academic Press, 1973), p. 450.

Figure 2. Plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for three different substrate temperatures.

The shift of ϵ_{OPT} from ~ 1.83 to ~ 1.63 eV as T_s changes from 215 to 415°C is largely responsible for the increased absorption as T_s increases. However, since the slopes are also gradually increasing with increasing T_s , either the density of states in the valence and conduction bands must be increasing or the transition probability must be gradually increasing.

It is likely that the variations of the optical properties with substrate temperature are related to the changing hydrogen content of the films. This hypothesis is supported by the fact that annealing of a film above its deposition temperature causes both the optical absorption and the hydrogen content to move toward the values expected for a film deposited at the annealing temperature.

3. Electrical Properties (Dark)

The conductivity of both undoped and doped a-Si films has been measured using a four-stripe Cr pattern on SiO₂. In the case of undoped a-Si films a thin Sb film was deposited on the Cr pattern prior to the a-Si deposition to assure good ohmic contacts.

In the low-field regime (10^2 - 10^3 V/cm) at temperatures of 30-200°C, the conduction is ohmic and thermally activated ($\sigma = \sigma_o e^{-E_a/kT}$). A recent discovery is that the pre-exponential term obeys the Meyer-Neldel rule, $\sigma_o = \sigma_{oo} \exp(E_a/kT_o)$, where σ_{oo} is a constant equal to $\sim 1 (\Omega\text{-cm})^{-1}$ and $T_o \sim 530^\circ\text{C}$. Figure 3 shows that a large number of doped samples obey this rule. Generally, E_a (or σ_o) decreases as T_s increases for a constant doping level. Since

$$\sigma = \sigma_{oo} \exp \left[- \frac{E_a}{kT} \left(\frac{T_o - T}{T_o} \right) \right] \quad (1)$$

and $T < T_o$, low values of E_a give more conductive films. The data in Fig. 3 show that PH₃ is the most effective doping source; organometallic vapors such as Sb(CH₃)₃ are poor sources, probably because of the inclusion of carbon in the films.

Undoped a-Si films also fall on the plot shown in Fig. 3. However, the conduction behavior in the dark is influenced by previous exposures to light and to elevated temperatures. The data shown in Fig. 4 illustrate the complexity of the conduction behavior for an undoped sample deposited at 320°C in an electroless rf discharge. When the film is heated to $\sim 200^\circ\text{C}$ and then cooled in the dark, the conductivity follows curve A. The sample is evidently in an equilibrium state since as long as it is kept in the dark, curve A is reversible. However, upon exposure of the sample to light at room temperature, the dark conductivity decreases; the magnitude of the decrease depends on the light intensity and exposure time. When the sample is heated in the dark, the conductivity follows curve B and is reversible for cycling to temperatures $\lesssim 100^\circ\text{C}$. Heating to $\sim 200^\circ\text{C}$ causes a transition from curve B to curve A within several minutes.

Both curves A and B fall on the plot of $\ln \sigma_o$ vs E_a shown in Fig. 3, so both σ_o and E_a change during exposure to light. The temperature T_o is that

Figure 3. $\ln \sigma_0$ vs E_g for n-type, a-Si films.

value at which all the conductivities are equal to σ_{00} or $\sim 1 (\Omega\text{-cm})^{-1}$; this temperature is evident in Fig. 4 by the intersection of curves A and B extrapolated to $\sim 530^\circ\text{C}$.

Exposure to light puts the films in a metastable conduction state; this causes some reduction in the lifetime as determined from photoconductivity measurements at low light levels. Diodes may also exhibit an increase in the dark series resistance due to the increased resistivity of a quasi-neutral region, but there is no change in the diode quality factor or the Schottky-barrier height. Data obtained from measurements of the photoconductivity and the photovoltaic properties of cells are characteristic of the metastable conduction state except when very low light intensities are used to probe an equilibrated film. The existence of this metastable conduction state does not

Figure 4. Conductivity as a function of reciprocal temperature for an undoped a-Si film.

appear to have any adverse effects on the stability of the solar cells (see Section II.E).

A comparison of the conductivity of p- and n-type films can give some information about the relative mobilities of the carriers. If it is assumed that the density of valence and conduction band states are comparable, then for films exhibiting the same values of E_a , $\mu_n/\mu_p \sim \sigma_n/\sigma_p \sim 5$, where this is a ratio of extended state mobilities.

4. Photoconductivity

The photoconductivity can be used to estimate the recombination lifetime, since the photocurrent is given by

$$i_p = q\phi_0(1 - R)[1 - \exp(-\alpha d)](\eta\mu\tau) \frac{\epsilon}{L} \quad (2)$$

where $\phi_0(1 - R)$ is the photon flux penetrating the film, α is the absorption coefficient for a given wavelength of light, d is the film thickness, η is the generation efficiency, μ is the carrier mobility, τ is the lifetime, L is the electrode spacing, and ϵ is the average electric field. The quantity $(\eta\mu\tau)$ is plotted in Fig. 5 as a function of photon energy for films deposited in an

Figure 5. $\eta\mu\tau$ as a function of photon energy for three different substrate temperatures.

electroless rf discharge at various substrate temperatures. If $\eta \sim 1$ at $h\nu \sim 2.0$ eV and $\mu \sim 5$ cm²/V-s, the lifetime is $\sim 5 \times 10^{-8}$ s for $T_s \sim 220^\circ\text{C}$ and increases to $\sim 3 \times 10^{-5}$ s for $T_s \sim 420^\circ\text{C}$.

The decrease in $\eta\mu\tau$ at high photon energies probably results from the nonuniform light absorption ($\alpha d \gg 1$) and the fact that the lifetime is dependent on light intensity. As the photon energy is decreased, a relatively

sharp drop occurs as $h\nu$ falls below ϵ_{OPT} . This falloff is due to a decreasing efficiency for the generation of electrons in the conduction band. The data for the film deposited at 420°C were not extended into the infrared due to a lack of absorption data in that region.

The hole lifetime has been estimated to be on the order of 10^{-6} s from photoconductivity measurements on lightly doped, p-type a-Si deposited from discharges containing 0.1% B_2H_6 in SiH_4 . For most films, at light intensities greater than 0.1 sun, the photoconductivity varies as the square root of the intensity; in this bimolecular recombination regime the electron and hole lifetimes should be equal.

Photoconductivity measurements were also made on films deposited from discharge atmospheres of 10% SiH_4 and 90% of either H_2 or D_2 . The lifetime was reduced by a factor of 10 for the SiH_4 - H_2 atmosphere and by a factor of 100 for the SiH_4 - D_2 atmosphere as compared with the lifetime of films made in pure SiH_4 at the same substrate temperature ($T_s = 330^\circ C$). An isotope effect was previously observed in the photoluminescence where the peak shifted up in energy by ~ 0.1 eV when D_2 rather than H_2 was used in the discharge atmosphere [3]. The degradation in lifetime is apparently due to the creation of new defect states (see Section II.C.1) and, in the case of films made in a SiH_4 - D_2 discharge, some defect states may shift toward mid-gap due to the stronger Si-D bond.

D. DEVICE CHARACTERISTICS

1. I-V Characteristics

Analyses of diode characteristics in far-forward bias in both the dark and in sunlight have shown that the resistance of the quasi-neutral region is a major contribution to the series resistance (especially in the dark). For undoped films deposited above $\sim 330^\circ C$, the photoconductivity of the a-Si in AM1 sunlight is sufficient to reduce the resistance of the quasi-neutral region to $\sim 1 \Omega\text{-cm}^2$ (for a 1- μm -thick film) [7]. Since the depletion region collapses in forward bias, the quasi-neutral region extends over most of the undoped film at operation in the maximum power mode.

An investigation of the forward bias conduction behavior at high voltages (1-15 V) and over a wide temperature range (77-300°K) suggests Poole-Frenkel conduction where the current density is given by

$$J = J_0 \exp \left(\frac{\beta_{PF} \epsilon^{1/2}}{kT} \right) \quad (3)$$

and where $\beta_{PF} = \left(\frac{\epsilon^3}{\pi K^* \epsilon_0} \right)^{1/2}$, K^* is the high-frequency dielectric constant and ϵ is the average electric field. Assuming that the average electric field is given by the Lorentz expression,

$$\epsilon \sim \left(\frac{K + 2}{3} \right) \frac{V}{d} \quad (4)$$

where K is the low-frequency dielectric constant, then a fit of Eq. (3) to the data gives values of $K^* \sim 9-13$.

The Poole-Frenkel effect is the field-assisted, thermal ionization of carriers out of coulombic traps. The lowering of the coulombic barrier by the field is given by $\Delta\phi = \beta_{PF} \epsilon^{1/2}$; this value is ~ 0.2 eV at the higher voltages, where the conduction mechanism appears to exhibit an avalanching behavior.

2. Surface States

Metals of varying work functions were used to deposit a series of Schottky barriers on both a-Si and single-crystal Si substrates. The surfaces were cleaned with buffered HF and a rinse in deionized water just prior to evaporation of the metals. The Schottky-barrier heights were determined by means of dark I-V data, plots of I_{sc} vs V_{oc} and C-V measurements. Figure 6 shows how the barrier height varies with metal work function for simultaneous evaporations of each metal on both a-Si and single-crystal Si.

A model proposed by Sze [9] is used to determine the density of surface states (D_s) from the slope of ϕ_B vs ϕ_M . For a-Si, $D_s \sim 2.8 \times 10^{13}$ states $(\text{cm}^2 \text{eV})^{-1}$ and for crystalline Si, $D_s \sim 3.1 \times 10^{13}$ states $(\text{cm}^2 \text{eV})^{-1}$. Thus,

9. S. M. Sze, *Physics of Semiconductor Devices* (Wiley-Interscience, New York, 1969), p. 372.

Figure 6. Schottky-barrier height vs metal work function for barriers on both crystalline and amorphous Si.

the surface state densities are similar. This may be due to the similarity of the short-range order in both materials [10] and to the existence of a similar type of interfacial layer on both surfaces. If no surface states were present, then ϕ_B would follow the dashed line shown in Fig. 6.

The barriers on a-Si are ~ 0.2 eV larger than on crystalline Si. This difference is probably due to a smaller electron affinity for a-Si.

3. p-Type Diodes

Because of better minority carrier diffusion lengths ($L_n > L_p$), diodes fabricated from lightly doped, p-type a-Si may exhibit better collection efficiencies at long wavelengths than diodes with undoped (n-type) a-Si.

10. M. V. Coleman and D. J. D. Thomas, "The Structure of Amorphous Silicon Films," Phys. Stat. Sol. 24, K111 (1967).

Preliminary results are encouraging for an Al Schottky-barrier cell with p-type a-Si on an Sb/Cr substrate. Although the series resistance increased with time, apparently due to the oxidation of the Al ($\sim 100 \text{ \AA}$ thick), the cell initially exhibited good values of V_{oc} ($\sim 650 \text{ mV}$) and J_{sc} ($\sim 2 \text{ mA/cm}^2$).

Capacitance-voltage measurements indicated that the cell was fully depleted in the dark ($d \sim 0.57 \text{ }\mu\text{m}$). Thus, the small concentration of boron is only slightly greater than that of the naturally occurring donor sites in undoped a-Si, and the material is almost fully compensated.

E. LIFE AND STABILITY TESTS

After 4400 hours of continuous illumination of $\sim 50\text{--}75 \text{ mW/cm}^2$, a Pd Schottky-barrier cell showed no degradation in conversion efficiency. Over the same period, an Ir Schottky-barrier cell exhibited a 25% decrease, and an Rh cell showed a 52% decrease in efficiency. All three cells were fabricated with $\sim 100 \text{ \AA}$ of the Schottky-barrier metal and no antireflection coating or passivation layer.

Secondary ion mass spectrometry (SIMS) was used to analyze an Ir Schottky-barrier cell as fabricated and, again, after one section had been heat treated for 15 minutes at 200°C in forming gas (90% N_2 , 10% H_2) and another section had been heated for 15 minutes at 200°C in air. The control sample exhibited $\sim 2 \text{ at. \%}$ of oxygen just beneath the metal/a-Si interface, a signal which fell by an order of magnitude over a few hundred angstrom. Heating in forming gas reduced the oxygen signal by $\sim 20\%$; the device showed an improvement in V_{oc} and a decrease in the series resistance. Heating in air caused the oxygen signal to increase by $\sim 30\%$ with respect to the control; V_{oc} decreased, while the series resistance increased. Other experiments have shown that the removal or reduction of oxygen near the surface leads to more stable devices [7].

An experiment with D_2O suggests water vapor to be the major source of degradation. Several Pt Schottky-barrier cells were placed in D_2O at 95°C for 15 minutes. V_{oc} fell from ~ 630 to $\sim 530 \text{ mV}$, and the series resistance increased by a factor of ~ 5 . A SIMS profile analysis showed $\sim 0.1 \text{ at. \%}$ of D_2O at the metal/a-Si interface. Moreover, portions of some Pt dots peeled off after the treatment in hot D_2O , suggesting that a hydrated layer forms at the interface and is seriously degrading the contact.

In future tests an antireflection coating of Si_3N_4 will be examined as a diffusion barrier for both oxygen and H_2O .

The stability of undoped a-Si films on several types of n^+ layers was examined by heating the structures for 15 minutes at 400°C in forming gas and then evaporating Ir Schottky barriers onto the top surface. Structures with a phosphorus-doped n^+ layer and Sb on Cr exhibited the best stability; in both cases the series resistance decreased as compared to that of control samples which were not heated to 400°C . Moreover, J_{sc} was not significantly affected by the heat treatment. In other structures, in which AsH_3 , $\text{Sb}(\text{CH}_3)_3$, and CsN_3 were used as dopants for the n^+ layers, J_{sc} decreased considerably after the heat treatment.

SECTION III

ANALYSIS OF RESULTS

The data presented in Section II.C.1 indicate that discharge-produced a-Si can be described as amorphous silicon subhydride, or $\text{a-Si}_{1-x}\text{H}_x$, where $0.02 \lesssim x \lesssim 0.16$. Since capacitance-voltage measurements indicate a low space-charge density ($\sim 10^{15}$ – $10^{16}/\text{cm}^3$), the bonded hydrogen must be compensating the dangling bonds normally found in evaporated or sputtered a-Si. Hydrogen should be an excellent dangling-bond terminator, since the Si-Si and Si-H bond strengths are similar (for diatomic molecules, the bond strengths are 3.30 and 3.24 eV, respectively).

Preliminary measurements of the density of discharge-produced a-Si indicate that ρ varies from $\sim 1.7 \text{ g/cm}^3$ for $T_s \sim 30^\circ\text{C}$ to $\sim 2.0 \text{ g/cm}^3$ for $T_s \sim 450^\circ\text{C}$. If the short-range order is similar to that of crystalline Si, then the difference in density from that of crystalline Si ($\rho \sim 2.33 \text{ g/cm}^3$) can be attributed mainly to microvoids. Assuming that the bonded hydrogen compensates all of the dangling bonds on the internal surfaces of the voids, one can estimate the average size and concentration of voids. For $\rho = 1.7 \text{ g/cm}^3$ and 16 at. % of bonded hydrogen (room temperature deposition), the microvoids have an average radius of $\sim 18 \text{ \AA}$ and a concentration of $\sim 10^{19}/\text{cm}^3$. For $\rho = 2.0 \text{ g/cm}^3$ and 3.5 at. % of bonded hydrogen ($T_s \sim 450^\circ\text{C}$), the average radius is $\sim 37 \text{ \AA}$ and the concentration is $\sim 6.5 \times 10^{17}/\text{cm}^3$. Thus, the analysis indicates that as T_s increases, the size of the microvoids increases but the concentration decreases.

Since divacancies in single-crystal Si pull the nearest neighbors inward by $\sim 0.25 \text{ \AA}$ [11], it seems likely that a large concentration of microvoids will decrease the average interatomic spacing as compared with single-crystal Si. Moreover, electron diffraction studies [10] suggest that the structure of discharge-produced a-Si is a mixture of diamond and dodecahedral structures with a lower density than crystalline Si. The above arguments suggest that the average radius of microvoids would be smaller than estimated and that their

11. H. J. Stein, "Defects in Silicon: Concepts and Correlation," in J. Corbett and G. Watkins, eds., *Radiation Effects in Semiconductors* (Gordon and Breach Science Publishers, London, 1971), p. 125.

concentration would be larger. In fact, one might expect the most common voids to be compensated vacancies and divacancies.

The compensated vacancy is probably stable in a-Si at room temperature, since four hydrogen atoms and one Si atom must jump simultaneously for it to move. (In single-crystal Si, vacancies anneal out at $\sim 150^\circ\text{K}$.) Photoluminescence may be due to the decay of excitons weakly bonded to compensated vacancies or divacancies.

The change in optical properties with increasing substrate temperature must be due to the changing structure of the films. The increase in the absorption coefficient and the refractive index with increasing T_s must be due to the decreasing hydrogen content and the increasing density, or equivalently to the changes in the average size and concentration of the microvoids.

The increase in the optical gap as the substrate temperature decreases may be explained by a dilated structure model [3]. As T_s decreases, the concentration of compensated voids increases, and the average dilational stress increases. This increasing dilational stress causes the band structure of crystalline Si to change so that the indirect bandgap moves further apart.

If compensated vacancies constitute most of the microvoids, then the concentration could be as high as $\sim 1.5 \times 10^{21}/\text{cm}^3$ (for 16 at. % H). This concentration corresponds to an average spacing of $\sim 8.7 \text{ \AA}$, and the electronic wave functions of these states would overlap to form a continuous band structure. The dipolar nature of the Si-H bond (2% ionic) will change the matrix elements for the optical transition probability as compared with those for crystalline Si.

The electrical properties are strongly influenced by defect states within the energy gap. Defects that might be expected from a logical extension of the above model would be partially compensated vacancies and divacancies (at least one dangling bond per void). Since singly ionized vacancies (V^+) and divacancies (VV^+) in crystalline Si have a level located approximately 0.3 eV above the valence band, ϵ_v , an ionized dangling bond in a partially compensated void in a-Si (V_{3H}^+) might have a similar level. The field effect measurements of Spear and LeComber [12] indicate defect states in discharge-produced a-Si at $\sim \epsilon_v + 0.35 \text{ eV}$ and at $\sim \epsilon_c - 0.4 \text{ eV}$, where ϵ_c represents the energy of the conduction band. The latter state may be associated with an electron attached to a

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12. W. C. Spear and P. G. LeComber, "Electronic Properties of Substitutionally Doped Amorphous Si and Ge," *Phil. Mag.* 33, 935 (1976).

partially compensated void (V_{3H}^-), since the negatively charged vacancy (V^-) and divacancy (VV^-) have levels at $\sim \epsilon_c - 0.55$ eV in crystalline Si.

Another defect that is likely to be found in discharge-produced a-Si is a partially compensated vacancy-oxygen defect (A'-center) similar to the A-center found in crystalline Si. Auger electron spectrometry and SIMS find oxygen concentrations varying from $\sim 5 \times 10^{17}/\text{cm}^3$ to $\sim 10^{20}/\text{cm}^3$ (~ 0.2 at. %) in discharge-produced a-Si, depending on the deposition conditions. In crystalline Si, the A-center is a negative charge center that has a level at $\sim \epsilon_c - 0.18$ eV. Drift mobility experiments in discharge-produced a-Si [13] indicate a trapping level at $\sim \epsilon_c - 0.18$ eV. The barrier lowering exhibited by the Poole-Frenkel effect also indicates a trap at $\sim \epsilon_c - 0.2$ eV (see Section II.C.3).

The partially compensated vacancies and divacancies may anneal out at low temperature ($\sim 200^\circ\text{C}$), and the reduction of these defects would cause an increase in the lifetime (see Section II.C.4). Annealing out of partially compensated voids could occur via motion of the voids to the surface or by complete compensation of all dangling bonds by interstitial hydrogen. Surprisingly, the diffusion constant of H_2 in a-Si appears to be relatively small; a value of $10^{-15} \text{ cm}^2/\text{s}$ was inferred from a SIMS profile of a sample heated for 15 minutes in D_2 at 200°C .

Since oxygen is present in the a-Si, some of the migrating voids may be captured to form A'-centers. Thus, the Fermi level would move toward ϵ_c as T_s or T_A increases due to the decreasing concentration of defects such as V_{3H}^+ and V_{3H}^- and the increasing concentration of A'-centers. This model is supported by experimental data and explains why undoped a-Si deposited at $T_s > 100^\circ\text{C}$ is n-type.

The infrared absorption data indicate that bonded hydrogen evolves from discharge-produced films that are annealed above their deposition temperatures (see Section II.C.1). The implication is that the concentration of compensated voids has a temperature-dependent "solubility" in discharge-produced a-Si.

The Meyer-Neldel rule ($\sigma_o = \sigma_{oo} \exp(E_a/kT_o)$; see Section II.C.3) may be due to a correlation between the amount of bonded hydrogen and the position of the Fermi level. The average density of conduction states near ϵ_c would have to

13. P. G. LeComber and W. E. Spear, "Electronic Transport in Amorphous Silicon Films," Phys. Rev. Letters 25, 506 (1970).

decrease as $|\epsilon_c - \epsilon_F| \approx E_a$ decreases, where ϵ_F is the Fermi level. Both effects could be due to the decrease in bonded hydrogen in fully and partially compensated voids. One possible explanation for the influence of light on the conduction mechanism is that photons create electrically compensating charge centers near both ϵ_c and ϵ_v , thus moving ϵ_F toward mid-gap while increasing the effective density of conduction states near the band edges.

The above arguments are supported by the fact that $\sigma \rightarrow \sigma_{00} \sim 1 (\Omega\text{-cm})^{-1}$ for all n-type films as the temperature, T , is increased toward 530°C . The bonded hydrogen content extrapolates to zero at roughly the same temperature (530°C) for either deposition or annealing (see Fig. 1). One could interpret Fig. 3 as predicting $E_a \approx |\epsilon_c - \epsilon_F| \rightarrow 0$ as $T \rightarrow 530^\circ\text{C}$, so that a correlation between the bonded hydrogen content and E_a could be inferred.

SECTION IV

SUMMARY AND RECOMMENDATIONS

Infrared absorption studies have shown that discharge-produced a-Si contains as much as ~16 at. % of bonded hydrogen for low-temperature depositions and that this value falls to ~2 at. % for substrate temperatures equal to ~500°C. The optical gap decreases and the absorption coefficient in the visible range increases as the concentration of bonded hydrogen decreases (at increasing T_s). The optical properties may be largely determined by the size and concentration of compensated microvoids (where hydrogen compensates all the dangling bonds on the internal surfaces).

The conduction behavior in the high-field regime ($\sim 10^4$ - 10^5 V/cm) appears to be due to the Poole-Frenkel effect or to the field-assisted, thermal ionization of carriers out of traps. At lower fields, the conduction is ohmic and thermally activated. However, the pre-exponential term, σ_0 , depends exponentially on the activation energy (and is temperature independent). This behavior may be related to the concentration of bonded hydrogen and its effect on the position of the Fermi level. Exposure to light creates a metastable conduction state that may be due to the creation of electrically compensating centers near the band edges.

The density of surface states has been estimated to be 3×10^{13} states $(\text{cm}^2 \text{ eV})^{-1}$ for both crystalline and amorphous Si.

Recent results on p-type Schottky-barrier diodes indicate that lightly boron doped a-Si is a good-quality solar cell material. Future efforts will be made to optimize this type of device as well as explore possible heterojunction cells made with lightly doped, p-type a-Si.

Emphasis will be placed on an optimization of the deposition parameters for the rf capacitive discharge system. A scale-up to 10 cm^2 for Schottky-barrier cells is now under way.

In view of the increasing complexity of the physics and chemistry of the material, we recommend that theoretical work be initiated in the areas of structural bonding and discharge-deposition kinetics. We continue to feel that a separate experimental study of the SiH_4 discharge would also be beneficial.

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