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AMORPHOUS THIN FILMS FOR SOLAR CELL APPLICATION

Final Technical Report, March 15, 1979—February 29, 1980

By

A. D. Jonath
W. W. Anderson
J. L. Crowley
H. F. MacMillan

F. A. Junga
J. F. Knudsen
K. M. Monahan
J. A. Thornton

March 1980

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Solar Energy

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3251 Hanover Street
Palo Alto, California 94304

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Section 1

INTRODUCTION AND SUMMARY

Magnetron sputtering, a deposition method in which magnetic confinement of a plasma encourages high deposition rates at low working gas partial pressures, is under investigation in this program as a candidate production technology for large-scale manufacture of high-efficiency, thin-film amorphous silicon solar photovoltaic cells. Our approach uses two dc magnetron geometries: (1) a low-cost planar magnetron (PM) system for exploratory and detailed examination of deposition parameter space; and (2) a cylindrical magnetron (CM) system, scalable to production sizes, for deposition of homogeneous films over large areas. Detailed descriptions of these two systems are included in Appendix A of this report.

During this first-year effort, amorphous silicon films and device structures were sputtered in both PM and CM systems under a wide range of deposition conditions (i.e., T_s , P_{Ar} , P_{H_2}) using both doped and undoped sputter targets. Measured electrical and optical film properties indicate that control over a wide range of conductivity, photoconductivity, conductivity activation energy, and optical and infrared absorption behavior is achievable. Analysis of film oxygen content and distribution profiles indicated that the severe oxygen inclusion by the growing films could be eliminated by a combination of pumping, trapping, and presputter gettering procedures. Films made under these precautionary conditions contain less than 0.1% oxygen.

Multiple depositions to fabricate simple MIS device structures and simultaneously to deposit monitor samples of individual constituent layers have been successful. Such MIS solar cell structures, using semitransparent gold Schottky contacts, have demonstrated photovoltaic behavior. While individual layers, especially the n^+ contact, have yet to be optimized, the projected best results to date are:

$J_{SC} = 3 \text{ mA/cm}^2$. Other program highlights are:

- Deposition rates as great as 1500 Å/min were achieved in high-power dc magnetron operation at practical substrate-target spacings.
- p-type and n-type a-Si:H consistently deposited from p- and n-type targets, respectively.
- Demonstrated correlation of argon and hydrogen partial pressure variations with optical, electronic, and structural properties of magnetron-sputtered a-Si:H films.
- Initial depositions have achieved properties comparable to those in films made by rf sputtering and glow-discharge methods.

The status of the work performed during this program and of the work remaining to be performed is given in section 2.5 (see Tables 2-2 and 2-3). Improvements in device design including field-aided collection of carriers that will optimize the a-Si:H solar cell are discussed in Section 3.

Section 2

RESULTS AND DISCUSSION

Both the planar and cylindrical magnetron systems were successfully employed to deposit a wide variety of amorphous silicon films during year one of this program. Optical, electronic, structural, and compositional measurements were used to characterize these films; variation of deposition parameters, subsequent ion implantation, and thermal anneal steps were observed to alter film properties. Some material suitable for first-generation solar cell development work was produced, but more importantly, a great degree of control over the deposition process variables needed to obtain this material was achieved.

The approach to and results of the sputter deposition aspect of the program to date is discussed in section 2.1. Problems, such as a resistivity of cylindrical silicon cathodes too great for dc operation and uncontrolled oxygen incorporation into growing films, were essentially eliminated. Elaborate fixturing has been incorporated into both planar and cylindrical systems to encompass depositions over broad substrate temperature range, sputtering, and reactive gas partial pressures, with various gas-phase or cosputtered alloying and doping elements and with provision for complete in situ device formation including metal evaporations.

Film and device properties are discussed in sections 2.2 and 2.4, and the ion implantation work is presented in section 2.3. Specific highlights are:

- Deposition rates as great as 1500 Å/min. were achieved in high-power dc magnetron operation at practical substrate-target spacings
- p-type and n-type a-Si:H consistently deposited from p- and n-type targets, respectively
- Demonstrated correlation of argon and hydrogen partial pressure variations with optical, electronic, and structural properties of magnetron-sputtered a-Si:H films

- Initial depositions have achieved properties comparable to those in films made by rf sputtering and glow discharge methods
- Film conductivity and photoconductivity modulated in H, P, and F ion implantation/anneal experiments.
- MIS structures which exhibit photovoltaic response were fabricated.

The remainder of the current program is summarized in section 2.5. Work in progress, items to be accomplished, postponed tasks, and additional efforts are listed therein.

2.1 DEPOSITION OF AMORPHOUS SILICON FILMS BY MAGNETRON SPUTTERING

The principal purpose of this investigation is to evaluate the application of magnetron sputtering to the fabrication of thin-film a-Si solar cells. The basic supposition of this investigation is that the cylindrical magnetron configuration is most amenable to scaleup for large-area deposition while the planar magnetron configuration is better suited to the preliminary exploration of deposition parameters. Hence, the planar magnetron is being used to establish the influences of deposition conditions on sputtered a-Si film and device properties. These results guide the selection of cylindrical magnetron sputtering conditions for experiments intended to demonstrate the practicality of large-scale deposition.

During the first year of this program, a versatile planar magnetron deposition system has been constructed at LMSC at no cost to the program. That system has just been completed, and the first a-Si deposition experiments are under way. The experiments planned for the remainder of this program in this system are outlined in section 2.4. The system is described in detail in Appendix A.

While the LMSC planar magnetron system has been under construction, a prototype of this system at Sputtered Films, Inc. (SFI) in Santa Barbara has been used for planar magnetron depositions of a-Si films. These depositions have provided invaluable experience for designing the LMSC planar magnetron system and for selecting the first cylindrical magnetron depositions. The rationale and conditions for these depositions.

are described in this section, followed by a discussion of the cylindrical magnetron depositions performed thus far. A detailed discussion of the film properties from both planar and cylindrical magnetron depositions is presented in section 2.2.

The SFI and LMSC planar magnetron systems have sputter sources called Research S-guns, which are manufactured by SFI. These sources use targets comprised of two concentric rings, slightly less than two inches in diameter, which produce a sputter flux distribution similar to that from a 2-in. planar target. At target-to-substrate distances of 2 in. or greater, uniformly thick films over areas greater than the prototype device size of 2-in. by 2-in. can be produced. For exploratory investigations, the 2-in. target diameter permits inexpensive targets to be fabricated from device-grade, single-crystal Si with a wide range of available dopants. Our first deposition experiments demonstrated that dc magnetron sputtering could be accomplished for target doping densities greater than 10^{15} cm^{-3} . This is a key result because the complexities of scaleup are much reduced for dc as compared to rf sputtering insofar as cathode configurations are concerned. Furthermore, dc sputtering has been obtained for target doping densities much lower than those expected to dominate in the deposited films. These first deposition experiments used p-type Si targets doped with 10^{16} and 10^{17} cm^{-3} B and n-type Si targets doped with 10^{15} and 10^{17} cm^{-3} Sb. Even though these doping densities are lower than those observed to dominate the conductivity of unhydrogenated a-Si films, the films deposited from these targets have always had the same conductivity type as their respective targets, as determined by thermoelectric power measurements. However, the relationship between magnitude of target and film conductivity has not been reproducible. The former results are surprising, but we have chosen not to pursue them at this time. The latter results suggest that gas phase doping during reactive sputtering should be more flexible and reproducible for device fabrication than doping directly from the target.

Almost all depositions in the SFI prototype chamber were made with the substrates mounted on a rotating carousel fixture. The carousel provides continuously varying target-to-substrate angles and distances, so that the resultant films have uniform thickness. Neither the instantaneous deposition rate nor the substrate temperature

is constant as the substrate moves in and out of the sputtering plasma. Control and measurement of film temperature is impractical as are in vacuo manipulations of samples and masks for multilayer device fabrication. These restrictions have limited the types of depositions that can be performed and have underscored the necessity for eliminating these limitations in the LMSC planar magnetron system.

Once dc sputtering was demonstrated, a series of a-Si depositions was made in which sputtering power was varied over a range from 500 W to 2 kW corresponding to average power densities at the target surface from 80 to 300 W/cm². The intent was to determine if film conductivities varied systematically with sputtering rate for p- and n-type targets. No systematic variation was observed. It has since become evident that variables uncontrolled in these depositions such as background water vapor pressure and substrate temperature were important parameters. These will be discussed shortly.

These depositions did provide other important information. Adhesion of films to glass and various metal substrates is excellent, if a glow discharge substrate cleaning step is incorporated prior to deposition. Secondly, film optical and conductivity properties are uniform from sample to sample and within one sample within the accuracy of measurement.

A second series of depositions was made in which H₂ was added to the Ar to investigate reactive magnetron sputtering deposition of a-Si:H. Depositions were made at three different flowrates of H₂: 1.5, 6.4, and 10.6 sccm mixed into a fixed 6-sccm flowrate of Ar, resulting in a partial pressure of Ar of 2 mtorr determined by thermocouple vacuum gauge. As expected, the films had increased resistivity and band gap with increasing H₂ flowrates. These depositions were followed by one deposition, at one intermediate H₂ flowrate and the usual Ar flowrate, onto fixed substrates at various target-to-substrate distances. These films showed a marked variation in Ar content from approximately 1/4 atomic percent for substrates 12 in. from the target to one percent for those 2 in. from the target.

Following these first two series of depositions, evaluation of film composition by SIMS, Rutherford backscattering, and Raman spectroscopy revealed that all of the films deposited to date had unintentional concentrations of up to 4-percent hydrogen and up to 15-percent oxygen. To verify that background water vapor in the deposition chamber was the source of these film contaminants, a third series of two depositions was made. Identical depositions were made in 2 mtorr Ar after an 18-h pumpdown to 8×10^{-7} torr and after a 2-h pumpdown to 3×10^{-6} torr. Films from the former deposition have oxygen content less than 1/2 atomic percent while films from the latter deposition have oxygen content of 4 atomic percent. The latter films also have a significantly higher energy absorption edge, which indicates greater hydrogen content. The pumpdown time for the latter deposition was typical of all of the earlier depositions.

The results of the latter depositions supported our contention that many of the variations in film properties observed in the earlier depositions were probably due to uncontrolled deposition conditions, especially background water vapor pressure. In addition, there was the lack of control and measurement of substrate temperature. Further depositions were postponed until the LMSC planar and Telic cylindrical magnetron systems became operational. Nonetheless, a wide range of film properties had been obtained, as discussed in section 2.2, and the need for rigorous control of sputtering gas purity had been highlighted.

The Telic cylindrical magnetron sputtering system used for depositions of a-Si and a-Si:H films is described in Appendix A. The deposition chamber has an array of substrates located 3 to 4 in. from the cathode, which is a water-cooled Si tube 15 in. long and 2-1/2 in. in diameter. A high-purity Wacker furnace tube formed by CVD of undoped Si and machined to precise size is used as a cathode target. The tube conductivity has been increased by neutron transmutation of Si to P followed by an anneal at 850 C in N_2 for 1 h to activate the P dopant, present at approximately 10^{14} cm^{-3} . The resulting conductivity is sufficient to permit dc magnetron sputtering, thereby avoiding the difficult design of satisfactory counter-electrodes required for rf sputtering. Preliminary deposition experiments at 1-mtorr Ar pressure demonstrated deposition rates of 150 Å/min and 300 Å/min at 1- and 2-A cathode currents, respectively. Higher deposition rates can be achieved, if it is deemed desirable, perhaps up to 1,000 Å/min.

Following the successful demonstration of dc cylindrical sputtering, a series of depositions of a-Si has been made at various Ar pressures and substrate temperatures. The purpose was to determine the effects of these parameters on structural, optical, and electrical properties and to establish the general relationship of these films to those deposited by planar magnetron and other methods such as rf diode sputtering and glow discharge in silane. The first depositions were made at Ar pressures of 1, 2, 3, 5 and 10 mtorr onto stress-plate substrates at 135 °C in order to evaluate internal stresses in the a-Si films. At the lowest Ar pressures significant compressive stresses were developed in the films, but for the 5 and 10 mtorr depositions the films had sufficiently small internal stresses that it was difficult to determine if they were compressive or tensile.

The next set of cylindrical magnetron depositions was made at 1, 10 and 30 mtorr Ar pressures onto substrates maintained at 135, 200, 300 and 400°C. All three depositions were made at a cathode current of 2 A and were intended to produce 0.5 μm thick films. The films deposited at 1 and 10 mtorr are uniform in thickness and in color. The films deposited at 30 mtorr are nonuniform in thickness and much thinner than the intended thickness.

Following this series, the first cylindrical magnetron deposition of a-Si:H films was made by reactive sputtering, in 10-mtorr Ar and 1-mtorr H_2 , onto substrates at 135, 200, and 300°C.

In all the foregoing depositions, a long presputter of Si was made to getter as much background O_2 and H_2O as possible. No oxygen has been detected in these films by Auger and electron microprobe analyses ($\text{O} < 0.1$ atomic percent).

The properties of these first cylindrical-magnetron a-Si and a-Si:H films (deposition series A in Table 2-3) are discussed in section 2.2.

The series B depositions incorporating Hydrogen in the a-Si films have been performed and preliminary MIS structures fabricated. The properties of these films and devices are discussed in sections 2.2 and 2.4 respectively.

2.2 FILM PROPERTIES

Characterization of a-Si:H films deposited during the first year of this program shows that we have obtained a wide variety of electro-optical properties in our films. Films have been produced which display properties comparable to those of films produced by other methods. Structural and atomic analysis shows that the bonding structure and chemical impurity content of reactive magnetron sputter films for solar cell devices is vulnerable.

Electrical Properties. The electrical properties of the a-Si:H films have been characterized by dark-conductivity and photoconductivity measurements made as a function of temperature. The dark conductivity for our films is thermally activated with activation energies of 0.14 eV to 0.70 eV. These films have room temperature conductivities that range from $4 \times 10^{-2} (\Omega\text{-cm})^{-1}$ to $10^{-10} (\Omega\text{-cm})^{-1}$. These wide ranges in magnitude for the room temperature conductivity and for the activation energy are the result of variation in controllable process parameters such as argon and hydrogen partial pressure and of unintended variations in oxygen and water vapor partial pressure. The latter two process variables along with substrate bias and temperature have been brought under control in the LMSC planar magnetron (PM) system and the Telic cylindrical magnetron (CM) system.

Figure 2-1 shows the thermally activated dark conductivity and photoconductivity for an a-Si:H film deposited in the prototype planar magnetron system where control of substrate temperature is not possible. The film has been annealed after deposition to observe the effect on conductivity. As the sample is annealed at higher temperature, the dark conductivity and the photoconductivity decrease but the decrease in the dark conductivity is more rapid than the decrease in the photoconductivity. The dark conductivity activation energy varies with anneal temperature and appears to represent a singly activated process. The photoconductivity appears to be more complex, with varying contributions from multiple processes as the anneal temperature changes.

Fig. 2-1 Thermally Activated Conductivity for an n-Type a-Si:H Film as Deposited and After Anneal at 300°C, 350°C, and 400°C for 10 min in Dry Argon (Photoconductivity Measured With Light Intensity of $25 \mu\text{W}/\text{cm}^2$ at 5300 Å.)

The first depositions in the CM system (series A in Table 2-3) were performed to test the operation of the polysilicon cathode and to determine the baseline properties of a-Si films sputtered without hydrogen. Figure 2-2 shows the room temperature resistance of these films as a function of the substrate deposition temperature. A resistance of $10^6 \Omega$ corresponds to a conductivity of $10^{-3} (\Omega\text{-cm})^{-1}$. The resistance for the a-Si films is a minimum for films deposited at approximately 200°C and a maximum for the films deposited at the highest substrate temperature (400°C). Auger analysis of these films failed to detect a measurable amount of oxygen. No photoconductivity was measured in any of the series A films and the dark conductivities were all thermally activated.

In Fig. 2-3 the dark conductivity and photoconductivity of an a-Si:H film deposited on a 200°C substrate in the CM system is shown. This film shows good photoconductivity under AM1 conditions. The photoconductivity activation energy for this film is similar to that for the film shown in Fig. 2-1. The conductivity versus temperature behavior for almost all of the CM a-Si:H films is qualitatively similar to that drawn in Fig. 2-3.

To compare the properties of the a-Si:H films from deposition series B (Table 2-3), consider the room temperature conductivity and photoconductivity as a function of the substrate deposition temperature. Figure 2-4 shows the room-temperature dark and photoconductivities for a-Si:H films deposited under $P_{\text{Ar}} = 10$ mtorr and $P_{\text{H}_2} = 1.0$ mtorr. There is a large increase in both dark and photoconductivity from the film deposited at 200°C to the film deposited at 100°C. The films deposited at 300°C had even higher dark conductivities but did not display any significant photoconductive response.

Figure 2-5 shows the room-temperature dark and photoconductivities for films deposited at $P_{\text{Ar}} = 1.5$ mtorr and $P_{\text{H}_2} = 1.0$ mtorr. The dark conductivities show a monotonic increase from the films deposited at 100°C to those deposited at 400°C. The photoconductivity, however, appears to have a slight maximum for films deposited at 300°C. This maximum in photoconductivity is believed to result from an increase in the number of photons absorbed due to the bandgap minimum observed in these films for $T_s = 300^\circ \text{C}$. This point will be considered further in the discussion of optical properties.

Fig. 2-2 Room Temperature Resistance as a Function of Substrate Deposition Temperature for Cylindrical Magnetron Film Deposited at $P_{Ar} = 1$ mtorr and $P_{Ar} = 10$ mtorr

Fig. 2-3 Thermally Activated Dark and Photoconductivity for a-Si:H Film Deposited in CM System ($T_s = 200^\circ\text{C}$, $P_{\text{H}_2} = 1$ mtorr, $P_{\text{Ar}} = 10$ mtorr)

Fig. 2-4 Room Temperature Conductivity as a Function of Substrate Deposition Temperature for Cylindrical Magnetron Film Deposited with $P_{\text{Ar}} = 10$ mtorr and $P_{\text{H}_2} = 1.0$ mtorr

Fig. 2-5 Room Temperature Conductivity as a Function of Substrate Deposition Temperature for Cylindrical Magnetron Film Deposited with $P_{Ar} = 1.5$ mtorr and $P_{H_2} = 1.0$ mtorr

Figure 2-6 shows the room-temperature dark and photoconductivities for yet another group of series B films, deposited at $P_{\text{Ar}} = 1.5$ mtorr and $P_{\text{H}_2} = 0.5$ mtorr. These films display a sharper photoconductivity maximum occurring at a lower T_s than the films discussed earlier (Fig. 2-5). This photoconductivity maximum at $T_s = 200^\circ \text{C}$ is accompanied by a maximum in room-temperature dark conductivity at the same deposition temperature.

Since a-Si:H depositions have just begun in the CM system, it is not possible to say what optimum properties of the films are achievable. However, the films deposited in the prototype PM system have contributed much toward executing successful depositions in the LMSC PM system and CM system.

Depositions of a-Si:H films were made in the prototype PM system using both p-type and n-type targets. The carrier sign for conduction in these films as determined by hot probe thermoelectric power measurements was p-type for film deposited with the p-type target and n-type for films deposited with the n-type target. On several p- and n-type films van der Pauw measurements were possible, and the carrier sign obtained from these measurements was consistent with that obtained from the thermoelectric power measurement. This result is contrary to the traditional carrier sign reversal reported for amorphous materials.

Optical Properties. The optical properties of a-Si:H films were determined from measurements of optical absorption and from the spectral response of the photoconductivity. The optical gap of the films is categorized by the film-color increases from metallic reflecting with no hydrogen content through red, red-orange, and orange-yellow as H_2 partial pressure during Si sputtering in argon is increased. It has also been determined that excessive oxygen content in some of the films caused them to appear orange-yellow.

Fig. 2-6 Room Temperature Conductivity as a Function of Substrate Deposition Temperature for Cylindrical Magnetron Films Deposited with $P_{\text{Ar}} = 1.5$ mtorr and $P_{\text{H}_2} = 0.5$ mtorr

The spectral response of the photoconductivity for the film whose thermally activated conductivity is plotted in Fig. 2-3 is shown in Fig. 2-7. The curve shows a sharp maximum above 2.0 eV. The rolloff of $\Delta\sigma/\phi$ at higher energies indicates that the measured conductivity is the true bulk conductivity and not surface conductivity-dominated. The data are consistent with those reported for other a-Si:H films.

The spectral response for films deposited at several substrate temperatures (100°, 200°, 300°, and 400°C) and P_{Ar}/P_{H_2} ratios (10/1 and 1.5/1) are drawn in Fig. 2-8. Since all the film thicknesses are equivalent, the position of the peak in spectral photo-response may be taken as an indication of the selective optical gap values among these films. The bandgap is thus seen to pass through a minimum for the 300°C deposition temperature. Therefore, the films deposited at the 300°C temperature will absorb more photons. This is consistent with the peak of the photoconductivity shown in Fig. 2.5 for the same films. Similar measurements for the films with P_{Ar}/P_{H_2} ratios of 1.5/0.5 (Fig. 2-6) are in progress.

Structural Properties. Microscopic and macroscopic film morphology, type and amount of hydrogen bonding, adhesion, and film stress have been measured for selected films. It has been observed for many years that vacuum-deposited silicon, produced either by sputtering or by evaporation, is in an amorphous state if the substrate temperature does not exceed about 700°C. To confirm that our a-Si:H films are amorphous, x-ray diffraction patterns of the films were obtained. The x-ray diffraction pattern displayed the broad ring image associated with amorphous films. Raman spectroscopy of the measurements on a few selected films confirmed them to be amorphous.

The infrared transmission spectrum of a-Si:H films was recorded by means of a Fourier transform infrared spectrophotometer (FTIR) to investigate the hydrogen bonding. Figure 2-9 shows a portion of the FTIR spectrum associated with the hydrogen bonding in the amorphous silicon. As seen in the figure, when the argon partial pressure is increased for these films deposited in the prototype PM system, the absorption shifts from a frequency associated with Si-H bonding toward a frequency associated with Si-H₂ bonding. This suggests that bonding structure may be controllable

Fig. 2-7 Spectral Response of Photoconductivity for a-Si:H Film Deposited in CM System ($T_s = 200^\circ\text{C}$, $P_{\text{H}_2} = 1$ mtorr, $P_{\text{Ar}} = 10$ mtorr)

Fig. 2-8 Peak of the Spectral Response of the Photocurrent for CM a:Si:H films as a Function of the Substrate Deposition Temperature (□ is deposited with $P_{Ar} = 1.5$ mtorr and $P_{H_2} = 1.0$ mtorr; ● is deposited with $P_{Ar} = 10$ mtorr and $P_{H_2} = 1.0$ mtorr)

Fig. 2-9 FTIR Spectrum of a-Si:H Films Deposited at Low (0.6 mtorr), Medium (2.0 mtorr) and High (3.5 mtorr) Partial Pressure of Hydrogen

using magnetron reactive sputtering. It has been noted, however, that the incorporation of oxygen in the film can also account for the shift in absorption frequency (Ref. 1).

Transmission electron microscopy studies of very thin films indicate that film nucleation and growth for the sputtered films is similar to that reported by Knights for glow-discharge-deposited films. Scanning electron microscope studies, however, are unable to distinguish any columnar morphology in the film cross section.

Finally, films were deposited in the cylindrical magnetron system at different argon partial pressures and the stress contained in the films was measured. For films deposited at argon partial pressures of less than 5 mtorr, the stress in the films is compressive. Films deposited at partial pressures of 5 and 10 mtorr are stressed only slightly if at all.

It is known that, when sputtered at lower argon partial pressures, the growing film is bombarded by energetic argon ions and is thereby compressed. Some of these argon ions are also trapped in the film. The amount of argon trapped in the film decreases with an increase in argon partial pressure. The compacted film and possibly the included argon is responsible for the compressive state. If the included argon is deleterious to device properties but the compacted film is not, we are prepared to sputter with a higher atomic weight gas which will serve to decrease the amount of sputtering gas trapped in the film. Measurements made on selected a-Si:H films using nuclear reaction analysis indicate that the density is 2.1 g/cm^3 (10 percent less than crystalline Si). This density is at the high end of the range of densities reported for hydrogenated a-Si (Ref. 2).

Atomic Composition of Films. In order to better understand the electro-optical properties of reactive magnetron sputtered a-Si:H, selected films have been analyzed for trace impurities using secondary ion mass spectroscopy (SIMS), Auger, electron microprobe, Raman spectroscopy, and Rutherford backscattering (RBS) combined with nuclear reaction analysis techniques.

The amount of hydrogen contained in our a-Si:H films was determined from Raman spectroscopy and IR transmission. One film which had not been intentionally hydrogenated but had displayed a large room temperature conductivity [$3 \times 10^{-3} (\Omega\text{-cm})^{-1}$] was found to contain 4 atomic percent hydrogen. It is thought that the hydrogen was incorporated as the result of water vapor in the chamber during sputtering. The Raman spectrum of this film is shown in Fig. 2-10. The hydrogen bonding appears to be solely Si-H as indicated by the stretch mode peak at 2000 cm^{-1} . The small peak near 970 cm^{-1} is the second-order amorphous silicon peak; the first-order peak is near 480 cm^{-1} .

SIMS analysis of films deposited with n-type or p-type targets have shown that the dopant in the target is effectively transferred to the sputtered film. This is consistent with the observation that films sputtered from an n-type target have an n-type carrier sign and films sputtered from a p-type target have a p-type carrier sign.

One impurity which received a great deal of attention in the characterization of our films was oxygen. This is because oxygen has been shown to be a dominant impurity in a-Si:H formed in a vacuum deposition (Ref. 3). The oxygen content of several films was profiled using a resonant energy (3.05 MeV) nuclear reaction technique. The magnitude of the oxygen concentration as determined by RBS was checked with electron microprobe and Auger measurements. The results of the oxygen profile for a typical early film are shown in Fig. 2-11. The oxygen concentration is seen to be higher near the back surface of the film. The back surface is the first material deposited during film growth and the higher concentration of oxygen could result from oxygen gettering at the start of the deposition. This film was deposited in the prototype PM system. Auger and electron microprobe analysis of films deposited in the CM system could not detect a measurable amount of oxygen ($>10^{18} \text{ cm}^{-3}$). Control of unintentional oxygen incorporation is also adequately designed for in the LMSC PM system.

Fig. 2-10 Raman Spectrum of Amorphous Silicon Film No. 61 Showing 2000 cm^{-1} Hydrogen Peak

Fig. 2-11 Oxygen Concentration Versus Film Thickness for a-Si:H (No. 95) Film

2.3 ION IMPLANTATION AND ANNEALING

Ion implantation was investigated as a complementary process technology to sputtering for the doping and alloying of a-Si and a-Si:H films. Monoenergetic doses of phosphorus (P^+), fluorine (F^+), and hydrogen (H_2^+) were implanted into a-Si and a-Si:H films at ambient temperatures. The energies of the implants were adjusted to give the maximum distribution of implant at the center of the film. The ion implantation parameters for the films in this study are given in Table 2-1.

Figure 2-1 shows the temperature-dependent conductivity for a hydrogenated sample prepared at 1-kW dc power with a partial pressure of approximately 2 mtorr of argon and 2 mtorr of hydrogen. This sample was selected because the as-deposited film displayed a slight amount of photoconductivity as shown in Fig. 2-1. After the initial measurement of the temperature-dependent conductivity, the sample was annealed at 300°C for 10 min in an argon atmosphere and the measurement repeated. Subsequent anneals were performed for 10 min in argon at 350°C and 400°C. As the sample is annealed at higher temperature, the dark conductivity and the photoconductivity decrease, but the decrease in the dark conductivity is more rapid than the decrease in the photoconductivity. The dark conductivity activation energy varies with anneal temperature and appears to represent a singly activated process. The photoconductivity activation appears to be more complex with varying contribution from multiple processes as the anneal temperature changes.

Figure 2-12 shows the temperature-dependent dark conductivity and photoconductivity for a phosphorus-implanted film (Table 2-1) with the same as-deposited characteristics as those shown in Fig. 2-1. Several points may be noted in comparing the implanted film with the as-deposited film:

- (1) The dark conductivity of the film is lower after the implantation
- (2) The absolute value of the photoconductivity is also lower after implantation although the percent change in conductivity under illumination is much greater
- (3) As the film is annealed to 400°C the dark and photoconductivity increase slightly

Table 2-1
ION IMPLANTATION PARAMETERS

Implanted Impurity	Dose (cm ⁻²)	Projected Range (μm)	σ_{ρ} (μm)	Concentration (cm ⁻³)			
				Average	Peak	At Front Surface	At Rear Surface
F ⁺	1 x 10 ¹⁶	0.285	0.110	2.50 x 10 ²⁰	4.0 x 10 ²⁰	1.0 x 10 ¹⁹	2.4 x 10 ²⁰
P ⁺	4 x 10 ¹³	0.160	0.056	1.25 x 10 ¹⁸	3.0 x 10 ¹⁸	3.0 x 10 ¹⁶	3.0 x 10 ¹⁶
H ₂ ⁺	5 x 10 ¹⁵	0.220	0.070	2.5 x 10 ^{20(a)}	6.0 x 10 ^{20(a)}	6.0 x 10 ^{18(a)}	1.5 x 10 ^{20(a)}

(a) Value for H⁺, assuming H₂⁺ dissociates during impact

Fig. 2-12 Thermally Activated Conductivity for a Phosphorus Implanted a-Si:H Film as Implanted and After Anneal at 300°C, 350°C, and 400°C for 10 min in Dry Argon (Film Deposited With a H₂ to Ar Partial Pressure of 1:1; Photoconductivity Measured With Light Intensity of 25 W/cm² at 5300 Å.)

- (4) The dark and photoconductive activation energies appear to be relatively insensitive to the annealing steps

Figure 2-13 depicts the temperature-dependent dark conductivity for a film with the same as-deposited characteristics as those in Fig. 2-1, but implanted with F^+ (Table 2-1) to a dose more than two orders of magnitude greater than the P^+ implant level. This film displayed no measurable dc photoconductivity, but as seen in the figure there is an increase of more than four orders of magnitude in the dark conductivity subsequent to implantation. The conductivity increases with anneal temperature in a manner similar to that in the P^+ implanted film. The dark conductivity mechanism appears to include multiple processes, as did the photoconductivity mechanism of the as-deposited film (Fig. 2-1). However, the variation of these activation energies with anneal temperature is nearly as restricted as in the P^+ implant case (Fig. 2-14).

Films deposited at low hydrogen partial pressure (0.5 mtorr) and without hydrogen (2×10^{-3} mtorr H_2O background chamber pressure) were also implanted and annealed. The latter samples were found via Raman spectroscopy to contain about 4 percent H bonded as $\equiv SiH$, and when F^+ -implanted showed negligible change in thermally dependent conductivity, activation energy, and anneal behavior. On the other hand, implantation of this very low H-content film with 1 percent H^+ (Table 2-1) acts to reduce the conductivity by an order of magnitude, followed by another order-of-magnitude decrease after a 10-min anneal at $300^\circ C$ in argon.

This finding is depicted in Fig. 2-14, which summarizes the implantation and anneal data. Unimplanted films (83 and 66) exhibit an increase of room temperature dark conductivity (RTC) with a $300^\circ C$ anneal temperature, as might be expected from decomposition of $\equiv SiH_2$ bonds. Photoconductivity data for sample 66 (not shown) also exhibit a maximum near 300° but then decrease subsequent to annealing at higher temperatures to $400^\circ C$. If $\equiv SiH$ bonds begin decomposing at the higher temperatures, one generally expects an accompanying increase in conductivity. However, Moustakas (Ref. 4) reports a similar result for the room temperature photoconductivity versus substrate temperature of films sputtered at a much lower

Fig. 2-13 Thermally Activated Dark Conductivity for a Fluorine Implanted a-Si:H Film as Implanted and After Anneal at 300°C, 350°C, and 400°C for 10 min in Dry Argon (Film Deposited With H_2 to Ar Partial Pressure Ratio of 1:1)

Fig. 2-14 Room Temperature Conductivity for $\alpha\text{-Si:H}$ Films as Deposited and as Implanted With F^+ (Suffix F), P^+ (Suffix P), and H_2 (Suffix H) as a Function of Anneal Temperature. Films were Deposited at H_2 to Ar Partial Pressure Ratios of 1:1 (Subscript M), 1:5.2 (Subscript L), or 0 (Subscript 0).

rate but under comparable H_2 and Ar partial pressures. His data imply that annealing at temperature can be substituted for depositing at temperature insofar as the "combined effect of network and hydrogen reorganization (in annealing) produces a film similar to the one deposited at high temperature." He relates the decrease in photoconductivity observed in these films above $250^\circ C$ to the stability of SiH_x groups at these temperatures.

Our results may be interpreted as adding corroborative details to this conjecture. The low hydrogen pressure films (83), identified in FTIR spectra as containing a predominance of $\equiv SiH$ bonds, exhibit the conductivity decrease at higher anneal temperatures than the medium pressure (66) or $\equiv SiH_2$ predominant films. This result is consistent with the observation that $\equiv SiH$ bonds are stable to higher temperatures than $\equiv SiH_2$ bonds and might indicate a network and hydrogen bonding reorganization effect on the conductivity at these anneal temperatures.

Such a network reorganization mechanism is offered to explain the hydrogen evolution experiments of McMillan and Peterson (Ref. 5) on glow-discharge produced films. According to this interpretation, $\equiv SiH_2$ centers decompose, forming hydrogen molecules. The heat released by H_2 formation is sufficient to break two Si-H bonds only when accompanied by local rearrangement of the silicon network to allow the exothermic creation of new Si-Si bonds. Thus, it might be argued that there is no net increase in gap states during $\equiv SiH_2$ center decomposition and that any attendant conductivity increase is related to mobility changes. McMillan and Peterson also determined that the $\equiv SiH$ center decomposition proceeds with lower activation enthalpy but with higher activation entropy. This finding suggests that network rearrangement processes may be more important in the H_2 evolution from $\equiv SiH$ than they are in $\equiv SiH_2$ decomposition. The very low H-content film 40 has no $\equiv SiH_2$ bonding, and thus any network and hydrogen bonding reorganization must proceed by a different mechanism.

Hydrogen evolution experiments have not been done on our samples, and the influence of magnetron sputter deposition on hydrogen bonding/evolution mechanisms remains

an open question. The complexity of such processes is indicated by the large change in conductivity activation energy and by the variation in conduction mechanisms with anneal temperature noted earlier (see Fig. 2-1).

The room temperature F^+ implant into a-Si:H (Fig. 2-14) increases the conductivity of both the low and medium hydrogen pressure films (87-1 and 67-1) by 4 to 5 orders of magnitude. The RTC variation with anneal temperature in these films is just the reverse of that in the unimplanted films discussed above. That is, the conductivity increases after anneal at temperatures above 300°C, and the conductivity activation energy remains nearly constant. The implantation damage either diminishes the $=SiH_2$ and $\equiv SiH$ bond density (no stretch modes for either are visible in the post-anneal spectra) or introduces additional defect states pinning the Fermi level. No doubt implantation damage plays a role in the silicon network rearrangement during H_2 evolution. Incorporation of implanted F has been confirmed by microprobe analysis, but full activation of the F has not been achieved in that no SiF modes are observed in the FTIR spectra. Perhaps the F implant acts to activate additional As present in the films. Additional annealing should be considered.

Similar annealing behavior was observed in the room temperature P^+ implantation (87-2 and 67-1). That is, RTC increases beyond the 300°C anneal temperature with nearly constant activation energy. This finding is contrary to the results reported by the Marburg group (Ref. 6) for P-implanted glow-discharge material. (Might these observations provide some insight into the differences between glow-discharge and sputtered material?)

There appears to be some post-anneal electronic activation of P in the low hydrogen pressure film (87-2). Why the implantation increases the RTC by more than two orders of magnitude in this film and decreases the RTC in the medium pressure film (68-1) remains to be explained.

It appears that film anneal and implantation anneal behavior are separable phenomena, but it is too early to claim understanding of either. (Further investigation under way includes Ne^+ and Ar^+ implantation to separate F or P activation from damage effects.) Dopant or alloy element activation is more efficient (Ref. 7) when implantation is at higher temperature, but it appears that gas phase and cosputtering should receive more attention as doping methods in the proposed program, and we recommend further ion implantation investigation be treated as a separate program

2.4 DEVICE CHARACTERIZATION

Simple semitransparent Au Schottky barriers have been formed on a-Si:H films deposited on stainless steel. The purpose of these Schottky barriers is to begin to characterize the properties of the intrinsic layer needed for the MIS or PIN device. The front surface contact is approximately 50 percent transmitting. Fig. 2-15 shows the I-V characteristic of one of the MIS structures. I_{SC} for this device is 0.5 mA/cm^2 under simulated AMI conditions. The best I_{SC} obtained so far is 0.7 mA/cm^2 . The front surface contacts are $2 \times 10^{-2} \text{ cm}^2$ in area, but the devices have displayed uniform I_{SC} response over the entire area of the films (6.25 cm^2). As shown in Fig. 2-15, much more photocurrent can be collected when the device is biased. The maximum biased photocurrent attained so far has been 3 mA/cm^2 , which could make our devices approximately 1 percent efficient. The Schottky barrier devices appear to have a blocking back-surface contact. Figure 2-16 is a calculated photo-response assuming that the device is really back-to-back photodiodes. The shape of the calculated curve agrees very well with the shape of the measured photoresponse. It is anticipated that the I_{SC} will improve when the blocking backcontact in the MIS device is eliminated. During the Series C depositions (Table 2-3), an n^+ contact layer will be deposited to the intrinsic layer.

2.5 TASK SUMMARY - CURRENT PROGRAM

The status of the current program in terms of the original statement of work is summarized in Table 2-2. Although several items have been rescheduled during

Fig. 2-15 AM1 Photo Response of a:Si:H Photodiode No. 169-34

Fig. 2-16 Theoretical Calculation of I-V Characteristic of Back-to-back Photodiodes

Table 2-2
CURRENT PROGRAM WORK STATEMENT STATUS

Task	Status	Task	Status
1. Theoretical Modeling (no scheduled work)	(See Task 5 below)	4. Schottky Barrier Photovoltaic Devices	Rudimentary Au-barrier devices fabricated - photovoltaic effect observed Pt barrier devices planned
2. Amorphous Thin Film and Doping			
(a) rf reactive sputtering	Counterelectrode problems solved. dc operation more practical		
(b) dc reactive sputtering	Accomplished		
(c) n-doped targets to produce n-type material	Accomplished (also p-doped targets used to produce p-type films)	5. Theoretical and Experimental Evaluation of Solar Cells	
(d) Phosphine gas-phase doping	Planned	(a) J_{sc} calculation based on absorption and minority carrier diffusion length data	Deleted
(e) Ion implantation of P, H, and Ni	Implantation of P, H, F, and B accomplished Ne and Ar implantations planned	(b) Optimized device structures designed, based on known material characteristics	Accomplished for test device (see section 2.2.1)
3. Film Characterization and Analysis		6. Additional Task (partly supported by 03-79-ET-23040)	Computer-aided data management system developed
(a) Optical absorption	Performed on selected films		
(b) IR absorption	Performed on selected films		
(c) Conductivity and photoconductivity versus T	Performed on selected films		
(d) Structural (electron and x-ray diffraction) and topographical (SEM) measurements	Performed on selected films		
(e) Schottky barriers for determination of:		7. Reporting	13 Technical Reports 2 Presentations 2 Papers submitted for publication
(i) Minority carrier diffusion length	Deleted		
(ii) Gap state density by C^{-2} versus V	Planned		
(f) Additional measurements (not specified in Statement of Work)	SIMS, Auger - microprobe for impurity determination in selected films. Also Raman. (Transient charge technique and deep-level transient spectroscopy under separate development)		

the course of the program, we have found it necessary to delete only two subtasks: 3ei and 5a. These relate to the minority carrier diffusion length, now accepted as so small in these materials that field-aided diffusion is required for any practical device (Task 5b).

Presently, cylindrical magnetron depositions are proceeding as shown in Table 2-3. Since the system can accommodate four substrate temperatures (or three when in situ Pt Schottky barrier deposition is required), series A, B, and C represent a total of 20 to 30 deposition runs.

A similar schedule will be used for depositions in the LMSC planar system, which is now under shakedown testing.

Table 2-3

DEPOSITION SCHEDULE AND RATIONALE BEHIND CURRENT CYLINDRICAL
MAGNETRON DEPOSITIONS

Deposition Series	Substrate Temperatures T_s (°C)	Argon Pressure p_{Ar} (mtorr)	H ₂ Pressure P_{H_2} (mtorr)	Objectives	Status
A	100, 200, 300, 400	1, 3, 5, 10, 30	0	Adhesion stress, p_{Ar} and σ versus argon content in films; check oxygen content and post-deposition oxidation	Completed (see sections 2.1 and 2.2)
B	100, 200, 300, 400	1, 3, 10	0.5, 1, 3	<ul style="list-style-type: none"> - Film photoconductivity versus P_{H_2} and T_s - Hydrogen incorporation and bonding - Preliminary MI and MIS structures for i-layer development 	In progress (see sections 2.1 and 2.2)
C	100 (and 2 higher T_s)	high, low	high, low	<ul style="list-style-type: none"> - Preliminary P_{H_3} doping - Plasma location effect on film properties - In situ Pt Schottky barriers 	March, April 1980

Section 3

EXPERIMENTAL SOLAR CELL DEVICE DESIGN: FIELD-ENHANCED MINORITY CARRIER COLLECTION

A schematic representation of the energy band structure of both a "Schottky barrier" and a "pn-junction" hydrogenated amorphous silicon (a-Si) solar cell is given in Fig. 3-1. In fact, the Schottky barrier is a Metal/Insulator/i-aSi/n⁺-aSi/Metal structure. In both cases, the dominant photoelectronic interaction of carrier generation and separation occurs in the i-aSi layer. The n⁺-aSi/Metal layers provide an ohmic back wall boundary condition for electrons. The role of the Metal/Insulator or the p-aSi layer is to induce a potential barrier for minority carrier charge collection or voltage generation. In the Schottky barrier example, the insulator layer is not essential to the basic device operation, but it does enhance the magnitude of the surface barrier potential. Development of the largest barrier potentials observed to date has been via an electrolyte contact (Ref. 8).

In Table 3-1 we indicate some of the better device characteristics reported for the various surface barrier contacts to i-aSi layers. The parameters listed on a single line in Table 3-1 do not necessarily refer to one device. Rather, they have been selected to indicate realized parameter limits to date. We will discuss some of the parameter interdependences in the following paragraphs.

From Table 3-1, we note the following strengths and problems of a-Si solar cells:

- Excellent open circuit voltage, V_{OC}
- Mediocre fill factor, FF
- Poor short circuit current, J_{SC}

Since the origin of J_{SC} is in the i-aSi layer, this layer will be the focus of our experimental program using either Schottky barrier or pn-junction devices as a matter of

Fig. 3-1 Potential Barrier Formation by Contacts to $i\text{-aSi}$

Table 3-1
 DEVICE PARAMETERS FOR VARIOUS a-Si SOLAR CELL STRUCTURES

	J_{SC}	V_{OC}	FF
pn-junction	7.33 ^(a)	0.797 ^(a)	0.507 ^(a)
Schottky barrier	12 ^(b)	0.865 ^(b)	0.61 ^(c)
Electrochem	4.5 ^(d)	1.25 ^(d)	—

(a) See Ref. 9.

(b) See Ref. 10.

(c) See Ref. 11.

(d) See Ref. 8.

convenience. The improvement of J_{SC} may be (somewhat) arbitrarily divided into optics problems and solid-state physics problems. Among the optics problems are:

- Front surface reflection losses
- Contact layer shadowing and absorption (includes band gap narrowing in this layer compared to i-layer absorption)
- Back surface reflection losses

Solid-state physics problems include:

- Carrier photogeneration
- Carrier collection/recombination

Our initial concern will be with the solid-state physics problems.

It was evident from early observations on the voltage and spectral dependence of photocurrent, $J_{Ph}(V, \lambda)$, that photocurrent generation and/or collection was electric field intensity dependent (Ref. 10). This may be due to either field-enhanced photoionization (Refs. 9 and 12) or field-enhanced minority carrier collection (Refs. 12 and 13). As a consequence, the device current/voltage relation must be written to include the voltage dependence of the collected photocurrent:

$$J = -J_{Ph}(V) + J_o \left(\exp \frac{q(V - JR_1)}{\kappa T} - 1 \right) + \frac{V}{R_2} \quad (3.1)$$

where:

- J $\equiv$ terminal current density
- J_o $\equiv$ saturation current density
- J_{Ph} $\equiv$ collected photogenerated current density
- V $\equiv$ terminal voltage
- $\kappa T/q$ $\equiv$ thermal voltage
- R_1 $\equiv$ series resistance ($\Omega\text{-cm}^2$)
- R_2 $\equiv$ shunt resistance ($\Omega\text{-cm}^2$)

The inclusion of voltage (field) dependence in the collected photogenerated current density results in a degradation in fill factor in addition to that due to parasitic resistances R_1 and R_2 ,

$$FF = FF(R_1, R_2, J_{Ph}(V)) \quad (3.2)$$

Thus, the mediocre fill factors in Table 3-1 are directly related to the poor short circuit currents and may be expected to improve with improved J_{SC} .

The two potential distributions indicated in Figs. 3-1a and b give rise to the electric field intensities

$$E = \begin{cases} \frac{-2V_D}{w} \left(1 - \frac{x}{w}\right) & \text{for } 0 \leq x \leq w \\ 0 & \text{for } x > w \end{cases} \quad (3.3)$$

when

$$w = \sqrt{\frac{2 \epsilon_r \epsilon_o V_D}{q N_D^*}} < t$$

and

$$E = -\frac{V_D}{t} + \frac{q N_D}{\epsilon_r \epsilon_o} \left(x - \frac{t}{2}\right) \quad \text{for } 0 \leq x \leq t \quad (3.4)$$

when

$$\sqrt{\frac{2 \epsilon_r \epsilon_o V_D^1}{q N_D^*}} > t$$

Equations (3.3) and (3.4) highlight the importance of a small effective donor density, N_D^* , and large diffusion potential, V_D (or V_D^1), to maximize the electric field intensity throughout the volume of the i-aSi layer, $0 \leq x \leq t$. Equations (3.3) and (3.4) are based on the fully depleted, uniform space charge layer approximation. The effective donor density, N_D^* , in the i-aSi case arises from a small difference between two mid-gap state distributions (Ref. 14). Minimizing midgap state density thus reduces N_D^* . The electric field intensity is a monotonically increasing function of V_D , linear in the Mott barrier limit of Eq. (3.4) or sublinear in the Schottky barrier described by Eq. (3.3). Maximizing diffusion potential increases photocurrent collection as well as exhibiting the usual effect on V_{OC} .

The continuity equation may easily be solved for holes in the Mott approximation ($E \approx -\frac{V_D}{t}$). The resultant expression for photocurrent is:

$$J_{Ph} = \frac{q \mu_P \tau_P V_D \alpha \phi_o}{\left[1 + \frac{\alpha \mu_P \tau_P V_D}{t}\right] t} \left[1 - e^{-\left(\alpha + \frac{t}{\mu_P \tau_P V_D}\right) t}\right] \quad (3.5)$$

for an incident photon irradiance, ϕ_o ($\text{cm}^{-2} \text{s}^{-1}$), and absorption constant, α (cm^{-1}). Note that Eq. (3.5) does not include a possible field dependence of photoionization. The total photocurrent to be used in Eq. (3.1) requires the integration of Eq. (3.5) over the solar spectral irradiance along with the spectral dependence of $\alpha(\lambda)$. Note that in Eq. (2.5) the usual minority carrier diffusion length dependence, $L_P = \sqrt{D_P \tau_P}$ has been replaced by a characteristic drift distance, $L_F = \mu_P \tau_P V_D / t$. Efficient

collection of photogenerated carriers occurs for $\alpha \mu_P \tau_P V_D / t > 1$, which highlights the importance of large α , large $\mu_P \tau_P$ products, and large collection fields $E \approx V_D / t$.

The materials program will concentrate on:

- Minimization of N_D^* (determined by gap state density)
- Maximization of $\mu_P \tau_P$ (also determined by gap state density)
- Adjustment of $\alpha(\lambda)$ (determined by H, F, and O content of aSi).

Within the constraints of the "best achievable" material parameters, it is possible to maximize J_{Ph} by

- An optimum thickness, t
- A back surface reflecting contact

The above discussion is illustrated by sample evaluations of the integral:

$$J_{Ph} = \frac{q \mu_P \tau_P V_D}{t} \int_0^{\infty} \frac{\alpha \phi \left[1 - \exp - \left(\alpha t + \frac{t^2}{\mu_P \tau_P V_D} \right) \right]}{1 + \frac{\alpha \mu_P \tau_P V_D}{t}} d\lambda \quad (3.6)$$

with the solar spectral irradiance approximated by:

$$\phi \approx \frac{4.41 \times 10^{18}}{\left[\exp(2.65/\lambda) - 1 \right] \lambda^4} \text{ Photons/cm}^2 \cdot \text{s} \cdot \mu\text{m} \quad (3.7)$$

The quality of the approximation in Eq. (3.7) is indicated in Fig. 3-2. The absorption coefficient of a-Si:H is nearly exponential with energy near the absorption edge (Ref. 2).

Fig. 3-2 Comparison of Analytic Model to AM1 Photon Spectral Irradiance

Therefore, we approximate the absorption characteristic by:

$$\alpha \approx \frac{5 \times 10^5}{1 + e^{6(E_0 - 1.239/\lambda)}} \text{ cm}^{-1} \quad (3.8)$$

We, along with other investigators, have experimentally determined that the absorption edge can be shifted via, for example, H content in a-Si:H. A convenient measure of absorption edge position is the wavelength at which the absorption constant is $\alpha = 10^4 \text{ cm}^{-1}$, i.e., $\lambda(\alpha = 10^4)$. This wavelength is variable over the range $0.6 \leq \lambda(\alpha = 10^4) \leq 0.85 \mu\text{m}$. In Fig. 3-3, we show this absorption edge variation superposed on the AM1 solar spectrum. It is apparent that the higher energy absorption edges miss a significant fraction of the AM1 spectrum photons. In Fig. 3-4, we show the strong dependence of short-circuit current on absorption edge position for the absorption edges in Fig. 3-3. The independent parameter in Eq. (3.6), $V_D \mu_P \tau_P$, was chosen as $5 \times 10^{-9} \text{ cm}^2$ for the calculations in Fig. 3-4. This corresponds to a diffusion potential of $V_D = 1$ volt and $\mu_P \tau_P = 0.5 \times 10^{-8} \text{ cm}^2/\text{V}$. In Fig. 3-5, we show the effect of variations in $V_D \mu_P \tau_P$. In both Figs. 3-4 and 3-5, a rather broad maximum exists for the optimum i-aSi:H active layer thickness, t . Also shown in Figs. 3-4 and 3-5 is a curve labeled " N_D^* Maximum" as a function of thickness, t . This is simply the requirement on depletion layer space charge density from Eqs. (3.3) and (3.4) for validity of the Mott barrier approximation to Eq. (3.4). Space charge layer densities down to $N_D^* \approx 5 \times 10^{15} \text{ cm}^{-3}$ have been reported (Refs. 10 and 11), but this appears to be reduced upon illumination. Hence, the collection width is likely to be less than $0.5 \mu\text{m}$.

The gain from increased short-circuit current associated with a lower energy absorption edge (Fig. 3-4) is partially offset by a reduction in diffusion potential. The effect of reduced V_D is shown in Fig. 3-5. We also note that, for active region voltages, $V_D \rightarrow V_D - V$ in Eq. (3.6), and that, from Fig. 3-5, the effect of J_{ph} (V) upon fill factor may be qualitatively understood.

In all cases, material and device parameters will be investigated in convenient solar cell device structures.

Fig. 3-3 Comparison of a Si:H Absorption Edge Positions to AM1 Photon Spectral Irradiance

Fig. 3-4 Maximum Short-circuit Current Collectable from a Mott Barrier with Absorption Edge Position as a Parameter

Fig. 3-5 Maximum Short-Circuit Current Collectable from a Mott Barrier With $V_D \mu_P \tau_P$ Product as a Parameter

Section 4
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Appendix A

PLANAR AND CYLINDRICAL MAGNETRON SPUTTERING SYSTEMS USED FOR a-SILICON DEPOSITION

The most significant feature of planar and cylindrical magnetron sputtering is the large sputtering rates that can be achieved because of the high power density in the plasma which is magnetically confined near the target. Even at high power levels, the plasma confinement results in reduced film heating and damage because of reduced electron and ion bombardment of the deposited film. High deposition rates permit greater production rates, and, perhaps more importantly, they proportionally reduce the undesired incorporation of ambient gas species. Doped Si targets are sufficiently conducting that dc sputtering can be utilized to achieve high deposition rates. Scaleup to production-size geometries should be much simpler using dc sputtering.

The principal thrust of this development effort is to demonstrate whether sputtering, especially magnetron sputtering, can be utilized to produce low-cost, high-quality, a-Si photovoltaic cells. While a cylindrical magnetron sputter system is more amenable to the deposition of large-area films, the planar magnetron sputter system is a more versatile and lower-cost development and research tool. Consequently, our strategy in developing a magnetron sputtering deposition process is to emphasize the selection and optimization of process variables using the planar magnetron. In conjunction, the cylindrical magnetron is being used to verify the potential for scaling up the deposition parameters to achieve comparable quality in large-area films.

A.1 PLANAR MAGNETRON SPUTTERING SYSTEMS

During the first year of this program, LMSC has been constructing a planar magnetron sputtering system at no cost to the program. This system, which is now undergoing preliminary testing, is specifically intended to provide versatility and relatively low-cost developmental depositions, which in turn will point the way for scaleup experiments in the cylindrical magnetron sputtering system.

The planar magnetron consists of a planar target from which sputtered material diverges slightly. Uniform coverage is limited to an area about the size of the target unless the substrates are mounted on a rotating planetary carousel in order to extend the area of uniform coverage at a reduced deposition rate. The advantage of small planar targets is ease and cost of fabrication. For a research-scale sputtering system, planar Si targets can be machined from device-grade, single-crystal Si wafers. Large cost savings and an extended range of doped Si materials are achieved; this is particularly important if a large variety of target dopings are to be investigated. In addition, high-purity metal targets for surveying potential contact metallizations are more available and far less expensive.

While the LMSC system was under construction, we have performed preliminary a-Si deposition experiments in a similar system at Sputtered Films, Inc. (SFI) in Santa Barbara, California. The SFI prototype system has the same sputtering targets (so-called Research S-guns) that are now in the LMSC planar magnetron sputtering system. Preliminary a-Si depositions have focused on establishing general trends in deposition parameters and film characteristics. Very valuable information has been provided for the detailed design of LMSC's system and for selecting the first cylindrical magnetron sputtering experiments.

The LMSC planar magnetron sputtering chamber is shown schematically in Fig. A-1. The chamber is entirely stainless steel to permit reactive sputtering with corrosive gases. It is moderately bakeable and has a liquid nitrogen cold wall in addition to the diffusion pump trap to minimize film contamination from background gases, particularly water vapor. There are positions for three Research S-gun sputtering devices which use 2-in. diameter annular rings as targets that are sufficiently large to deposit uniform films over a 2-in. by 2-in. area for prototype device fabrication. Although it is intended to use dc sputtering for easier scaleup whenever practical, provisions for rf sputtering have been included. There are also three independent thermal evaporation boats for use in fabricating multilayer photovoltaic devices without interrupting vacuum.

Argon is the primary sputtering gas. The inlet gas manifold permits precise flow control of argon and up to six additive gases for reactive sputtering, especially H_2 , PH_3 , B_2H_6 ,

A-3

Fig. A-1 LMSC Planar Magnetron Sputtering System

SiF_4 , and O_2 . The sputtering ambient will be monitored with an absolute pressure manometer and a residual gas analyzer. Constant sputtering pressure (in the 1- to 20-mtorr range for the research S-gun) is maintained with a variable orifice at the inlet to the oil diffusion pump below the diffusion pump liquid nitrogen trap.

At sputtering pressures in the 10-mtorr range, the purity of available gases establishes the background partial pressure of unintentional impurities, especially water vapor, at a maximum of 3×10^{-8} torr in the sputtering gases. This is comparable to total pressures of 8×10^{-8} torr achieved in preliminary pumping experiments on the newly assembled chamber. For normal sputtering powers in the range 1/2 to 2 kW, the deposition rates of a-Si are sufficiently high that we anticipate unintentional impurities incorporated in the films to be less than 0.1 atomic percent.

Substrates are mounted above the targets on a platform which adjusts for a wide range of target-to-substrate distances. The platform will generally not rotate during deposition, so maximum deposition rates can be achieved. The platform is electrically isolated, so glow discharge cleaning of substrates can be accomplished. In addition, the platform can be rf-powered and dc-biased to establish a plasma at the deposition surface enriched in desirable ions such as H^+ , F^- , P^- , or B^+ , for the purpose of tailoring a-Si film properties.

Just above the substrate platform at each sputter gun location there is an infrared lamp to enable control of substrate temperature up to 600°C during deposition and for post-deposition annealing. The substrate platform is split-level so that only the desired substrate is heated by infrared lamp or sputter gun.

All of these features are included to provide control over deposition parameters which are expected to strongly influence the electrical and optical properties of a-Si and a-Si:H films.

A sample and mask pick-up arm enables sequential depositions on different substrates from the same sputtering source, as well as sequential depositions of different films through different masks onto the same substrate. The various deposition sequences that can be achieved during the same pumpdown are limited only by the three target materials,

Fig. A-2 In Vacuc Fabrication Process for Amorphous Silicon PIN Solar Cell

Fig. A-3 Schematic Illustration of Cylindrical Magnetron Sputtering Source

three evaporation boats, and sample and mask storage space on the substrate platform. As an example, a six-step deposition of an a-Si solar cell, which can be accomplished in the LMSC system without interrupting vacuum, is depicted in Fig. A-2. A very important feature of the sample manipulator design is that it permits, with proper mask design, deposition of multilayer devices and simultaneous deposition of the individual component layers of the device so that each can be investigated separately. There are also provisions in the sample frames and chamber for monitoring film temperature and electrical conductivity throughout the deposition process.

A.2 CYLINDRICAL MAGNETRON SPUTTERING SYSTEM

Cylindrical magnetrons can also be scaled to very large size for large-area film depositions such as the one shown schematically in Fig. A.3 (see Appendix B). The relatively large targets used even in modest-size cylindrical magnetrons are very costly for preliminary survey experiments on optimizing a-Si film properties. However, since several features of the cylindrical magnetron recommend its eventual use for sputtering large-area a-Si photovoltaic cells, investigations with a limited variety of Si targets have been initiated. These attractive features include the following considerations.

The uniform current density on the target surface means that surface chemistry reactions occur uniformly over the target surface. This is an important consideration in achieving spatially uniform coatings. The overall cylindrical symmetry eases the problem of uniformly injecting the reactive gas, which is an important consideration at high deposition rates. Furthermore, the incident flux of coating material can be made to be primarily normal to the substrate surfaces. The coating flux arrival direction exerts a significant influence on the structure of vacuum-deposited coatings.

Sputtered a-Si:H coatings deposited in first-generation planar systems have tended to consist of a mixture of the desirable monohydride and undesirable dihydride forms. By comparison, cylindrical magnetron sputtering sources can be operated at relatively low pressures (< 1 mtorr), so volume reactions between H^+ ions that produce the dihydride are very rare. As the apparatus size is made larger, the allowable operating pressure is reduced even more. When a cylindrical magnetron is operated

Fig. A-4 Cylindrical Magnetron Deposition Chamber Cross Section Showing Substrate Holder Arrangements and Pt Minicathode Location

at low pressures with a low-mass reactive gas, a relatively intense beam of atomic reactive gas species is generated at the cathode and passes along with the target coating material to the substrate. Thus, the cylindrical geometry is expected to be very effective for incorporating low-mass monohydride ions into a growing Si coating.

The cylindrical megnetron system at Telic (Fig. A-4), which is used for deposition of a-Si and a-Si:H, has a 15-in.-long, 2-1/2 in. O.D. hollow cylinder target, which can be machined from a Czochralski-grown, single-crystal boule or from a CVD-grown Si furnace tube.

DC magnetron sputtering has been achieved using a high-purity, CVD-grown tube that has been neutron-transmutation doped with P to reduce the target resistivity.

Multiple substrate mounting posts are distributed around the chamber perimeter at a constant radius from the target. Each substrate mount can be maintained at a different deposition temperature and individually rotated to initiate and terminate deposition. A multiple-gas manifold provides a mixture of argon and selected gases for reactive sputtering of a-Si in H_2 , PH_3 , and B_2H_6 . A second target cathode has been substituted at one substrate post location for sputter deposition of a metallization layer(s) or a barrier metal. Thus, even though masks cannot be manipulated in vacuo, simple MIS and P^+-I-N^+ device structures can be fabricated without interrupting vacuum.

The chamber is pumped by a cryogenic-trapped oil diffusion pump with variable orifice for maintaining constant sputtering pressure. The base pressure of the system is 10^{-6} torr, which seems rather high except that the total sputtering flux of Si from the large target is also very large. Films of a-Si and a-Si:H deposited thus far have no unintentional impurities (< 0.1 atomic percent) detectable by Auger and electron microprobe analyses.