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AMORPHOUS THIN FILMS FOR SOLAR CELL APPLICATION

MASTER

Quarterly Report No. 1 for March 31—June 30, 1979

By

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July 1979

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Solar Energy

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FOR
SOLAR CELL APPLICATION

Quarterly Report No. 1
For Period
March 31, 1979 - June 30, 1979

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Section 1

INTRODUCTION AND SUMMARY

The prospects for generation of significant electric power using low-cost photovoltaic solar cells seem brighter with recent developments in sensitive impurity doping of glow-discharge-produced films of amorphous silicon containing large amounts of hydrogen (a-Si:H). With such films, small area photovoltaic solar cells of nearly 6% efficiency have been fabricated. This significant accomplishment establishes, as a goal for this program, the development of 10% efficient amorphous silicon solar cells utilizing methods adaptable to large-scale, low-cost production.

The approach being taken to achieve the program objective centers on substituting sputtering for glow-discharge in the deposition of the a-Si:H films. Sputtering technology is an established production process for a variety of large-area metal and insulator coating needs and is rapidly expanding from infancy through innovative stages in the deposition of solid state coatings and films. Whereas glow discharge deposition includes both volume and surface reactions, sputtering deposition proceeds primarily by surface reactions. Thus, in principle, problems associated with scale-up and controllability of film properties are simplified in the sputtering method.

Both planar and cylindrical forms of magnetron sputtering are being investigated in this program. Brief descriptions of the systems being used are included in Section 2.1. The planar system has the advantage that experimental costs are low; the cylindrical system is easily scalable to large product throughput. A-Si:H films are being prepared by magnetron sputtering, with reactive gases and/or doped Si targets, to achieve a reproducible and controllable process for the fabrication of solar cell devices.

Ion implantation is being used for alloying and doping studies. This allows for a rapid and systematic survey of alloy materials, such as H, F and transition metals, for reducing mid-gap states, and also dopants, such as B, P and As, for conductivity control. In addition to being a flexible exploratory tool, ion implantation also has the potential for incorporation into large-scale production processes.

The first quarter program plan emphasis was on film deposition, ion implantation and characterization. The observations and results to date are summarized as follows.

1. N- and p-type a-Si and a-Si:H films are consistently deposited on a variety of substrate materials from n- and p-type silicon single-crystal sputter targets respectively.
2. A-Si (without intentional hydrogen incorporation) and a-Si:H films exhibit thermally activated conductivity.
3. A-Si:H films are 3 to 5 orders of magnitude more resistive than the a-Si films.
4. The optical gap of the films as categorized by the film color increases from metallic-reflecting at no H_2 through red, red-orange, and orange-yellow as H_2 partial pressure during Si sputtering in argon is increased.
5. Si-H and Si- H_2 hydrogen incorporation as observed by Fourier transform infrared spectroscopy can be adjusted by modulating hydrogen reactive gas pressure in the planar sputtering system. (No data on this in the cylindrical system as yet.)
6. Small photoconductivity has been observed in several a-Si:H films.
7. Room temperature ion implantation of a-Si films with H^+ , F^- as alloying elements and P^- as dopant yields conductivity modification even before the films are annealed.
8. "Grain-like" structure of 500 Å scale is observed by transmission electron microscopy in a high conductivity a-Si film.

No device work was scheduled during this reporting period and only rudimentary junction structures were fabricated to test sequential deposition procedures. The theoretical modeling task is complete. The work presented in our proposal, LMSC-D085209, May 1978, in response to PRDA ET-78-R-03-1846 adequately supports the first year's program.

A data management system is being implemented to assist in keeping track of the large number of samples that will be deposited, analyzed, implemented, reanalyzed, etc. in this program. The Xerox Sigma 5 computer in the Missile Systems Division of LMSC has been made available for this need.

Section 2

FILM AND DEVICE PREPARATION

As described in the preceding section, 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 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. Subsequently, the cylindrical magnetron must be used to verify the potential for scaling up the deposition parameters to achieve comparable quality in large area films.

The most significant feature of magnetron sputtering is the large sputtering rates which can be achieved because of the high-power density in the plasma that is magnetically confined near the target. Even at high-power levels the plasma confinement results in reduced film heating and damage due to 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. Scale-up to production size geometries should be much simpler using DC sputtering.

2.1 DESCRIPTION OF DEPOSITION SYSTEMS

Both planar and cylindrical magnetron sputtering systems have these potentially advantageous characteristics. The particular advantages of each system will be described in turn.

2.1.1 Planar Magnetron Sputtering Systems

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 which extends the area of uniform coverage at a much 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 available Si materials are achieved; this is particularly important if a large variety of target dopings are to be investigated.

LMSC has consequently decided to construct a planar magnetron sputtering system using 2" O.D. target disks which are sufficiently large to deposit uniform films over a prototype size 2" x 2" substrate area.

While this system is 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) which will be in the LMSC planar magnetron sputtering system. The SFI system is not sufficiently flexible for development of an optimum film deposition process. Therefore, preliminary a-Si depositions have focused on establishing general trends in deposition parameters and film characteristics. Also, valuable information has been provided for the detailed design of LMSC's system, and for selecting the first cylindrical magnetron sputtering experiments.

The LMSC system, which is now under construction at no cost to this program, is depicted schematically in Fig. 1. The system has a bakeable stainless-steel chamber with a liquid nitrogen cold wall to minimize film contamination from background gases, particularly water vapor. There are positions for three sputtering targets so a multi-layer photovoltaic device can be fabricated without interrupting vacuum. The targets can be DC or RF sputtered. Argon will be the working gas, and provisions for

Fig. 1 LMSC Planar Magnetron Sputtering System

reactively sputtering in mixtures of H_2 , O_2 , N_2 , PH_3 , B_2H_6 and SiF_4 are included. The sputtering ambient will be monitored with an absolute pressure manometer and residual gas analyzer.

Substrates are mounted on a platform which adjusts for a wide range of target-substrate distances and substrate heating to $500^\circ C$ during deposition. The platform will generally not rotate during deposition, so maximum deposition rates can be achieved. A sample pick-up mechanism will enable sequential depositions on different substrates during the same pumpdown, as well as sequential depositions of different films through different masks onto the same substrate. 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 those of H, F, P, B or O, for the purpose of tailoring a-Si:H film properties.

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

The SFI prototype system has a rotating planetary carousel which has several shortcomings for our purposes. The average deposition rate is much lower than the peak instantaneous rate, so deposition times are longer and film properties may vary across the film thickness. Film temperature cannot be controlled or measured during deposition. More importantly, only one deposition condition can be tested during a single pumpdown. Hence it requires many more pumpdowns to establish the effects of varying deposition parameters on film properties.

2.1.2 Cylindrical Magnetron Sputtering System

Cylindrical magnetrons can be scaled to very large size for large area film deposition such as the one shown schematically in Fig. 2. For example, Telic Corporation has a 9-ft long cylindrical target used for depositing 70 ft^2 films. The relatively large

Fig. 2 Cylindrical-Post Magnetron Reactive Sputtering System Schematic

targets used even in modest size cylindrical magnetrons are very costly for preliminary survey experiments on optimizing a-Si film properties. However, several features of the cylindrical magnetron recommend its eventual use for sputtering large area a-Si photovoltaic cells, so investigations with a limited variety of Si targets are being 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 ($< 1\text{-m Torr}$), 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 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 magnetron system at Telic which will be used for deposition of a-Si and a-Si:H has a 15 in. long, 2-1/2 OD target which can be machined from a single-crystal Si boule, a CVD-deposited tube, or cast from the melt. There are provisions for varying substrate temperature and admitting a mixture of reactive gases such as H_2 , PH_3 and B_2H_6 . Multiple substrate mounting locations are incorporated

as shown schematically in Fig. 2. A second (smaller) cathode is provided at one substrate longitude-position for sputter deposition of a barrier metal. Thus, a device structure can be fabricated without breaking vacuum.

2.2 FILM DEPOSITIONS AND ION IMPLANTATIONS

In this section, the material preparations during this quarter are described. Procedures for deposition of a-Si and a-Si:H films by planar magnetron sputtering, for electrical contacting to deposited films and for ion implantation of deposited films are described.

2.2.1 Film Depositions

All a-Si films have been deposited in the prototype planar magnetron system at Sputtered Films, Inc.

The strategy for these preliminary sputtering experiments has focused on establishing general trends in deposition parameters and film characteristics.

Sputter targets were machined from p- and n-type Czochralski grown single-crystal Si wafers. The targets are sufficiently conductive even for low doping concentrations (e.g., B, As $> 10^{14} \text{ cm}^{-3}$) to permit DC sputtering, a great simplification compared to RF sputtering necessary for low-conductivity targets.

Deposition rates were controlled by varying DC power in the plasma over the range of 0.2 to 2 kW. The pressure of the argon sputtering gas was maintained constant during deposition in the range 1 to 10 m Torr. For the reactive sputtering preparation of a-Si:H films, H_2 gas was mixed with Ar prior to introduction into the chamber. The relative partial pressures of Ar and H_2 could not be measured accurately; instead, the mass flow rate of each gas was measured and maintained constant during deposition.

Intentional doping of the films has been accomplished by using doped Si target material. A SIMS (secondary ion mass spectrometer) analysis of target and film materials qualitatively confirmed the efficient transfer of intentional and unintentional dopants from target to film for both B- and As-doped Si. The analysis conditions were not sufficiently controlled to permit quantitative comparisons of target and film compositions. Doping of a-Si films by reactive sputtering with PH_3 or B_2H_6 to provide P or B gas-phase doping will be attempted during the next quarter.

Amorphous Si and a-Si:H were deposited on a variety of insulating and metallic substrates. Adhesion was excellent to all metal surfaces except Au even without particular cleaning. Good adhesion to Corning 7059 glass, quartz and sapphire depended on glow discharge cleaning in O_2 prior to deposition, even after very particular cleaning with detergents, acids and/or solvents.

Substrates were mounted for deposition in a carousel which provides very uniform film thickness over all substrates. Film thickness measurements by Sloan Dektak profilometer showed good thickness uniformity and repeatability among different substrates. Variations in electrical conductivity between substrates was less than 30 percent.

The average deposition rates were in the range 20 to 200 Å/min for films sputtered at 0.2 to 2 kW power. The peak instantaneous deposition rates are estimated to be more than a factor of ten greater. The carousel causes the deposition rate to vary cyclically during a deposition. The influence of this variation on film properties is under investigation. The carousel does not permit control or measurement of substrate temperature during deposition. All depositions have been performed with no substrate heating beyond that provided by the sputtering plasma and plasma heated target. The substrate temperature during deposition was estimated to be 50° to 100°C. Investigations of the influence of substrate temperature will be undertaken next quarter.

In summary, during the first quarter, about one hundred different a-Si and a-Si:H samples have been deposited. Si targets with 10^{17} cm^{-3} As and 10^{17} and 10^{14} cm^{-3} B doping have been used. A limited range of the Ar sputtering pressure of about 2 m Torr was used over a range of sputtering powers from 0.2 to 2.0 kW. The pressure of H_2 has been varied from zero to 1.5 times the Ar pressure (~ 3 m Torr). Films from 1000 Å to 1.3 μm thickness have been deposited on one or more of a variety of substrates: 7059 glass, quartz, sapphire; Mo, Al, Ti, Au, and stainless steel.

For electrical conductivity measurements, a "four-point" array of metal contacts are utilized to minimize errors due to contact resistance. Contact arrays have been applied by evaporation through a shadow mask, either onto the deposited a-Si film or onto the insulating substrate prior to film deposition. Either procedure gives identical results, but the former procedure avoids the difficulties arising from poor adhesion of the metal contacts to the insulating substrate. Al, Au, In and Cr have been compared as contact metals. For all metals, the four-point conductivity measurements gave the same results for both p- and n-type a-Si films, but none of them provided low-resistance ohmic contact to p- or n-type films. Au has generally been used because of a combination of acceptable contact I-V characteristics and ease of evaporation. We plan to compare sputter-deposited Mo, Cr and stainless steel contacts in the next quarter.

2.2.2 Ion Implantation Alloying and Doping

Preliminary ion implantations have been made into a-Si films. The primary purposes of these first implantations is to refine the associated experimental procedures and to verify that significant changes in film properties can be achieved. These implantations were conducted at room temperature. The effects of film temperature during implantation and during post-implant annealing will be investigated in the next quarter.

All ion implantations are performed in an Accelerators Inc. commercially supplied ion implantation facility intended for integrated circuit implantations. The useful beam energy range is 20 to 400 keV at beam fluxes from 1 to 50 μA . The implantations are performed in vacuum at pressures below 5×10^{-6} Torr. The sample carousel has provisions for heating samples to 300°C during deposition.

Implantation alloying has been attempted by implanting approximately one atomic percent H or F into conducting n-type a-Si films doped with 10^{17} cm^{-3} As. The purpose is to investigate the utility of implanting H or F to reduce the large density of states in the mobility gap of a-Si.

Implantation doping has been attempted by implanting approximately 10^{18} cm^{-3} P into n-type a-Si films doped with 10^{17} cm^{-3} As and 10^{18} cm^{-3} B into p-type a-Si films doped with 10^{17} cm^{-3} B. The purpose of these implantations is to investigate the utility of implanting dopants to achieve highly conducting p- and n-type contact layers for photovoltaic devices and to investigate the properties of dopants in a-Si.

Table 1 presents the ion-implantation parameters for these first alloying and doping implantations. For simplicity these implants were monoenergetic. The values of

Table 1
ION IMPLANTATION PARAMETERS

Sample No.	Implanted Impurity	Sample Thickness (μ)	Dose (cm^{-2})	Projected Range (μ)	σ_p (μ)	Concentration (cm^{-3})			
						Average	Peak	At Front Surface	At Rear Surface
36-2	F ⁺	0.40	1×10^{16}	0.285	0.110	2.50×10^{20}	4×10^{20}	1×10^{19}	2.4×10^{20}
36-1	H ₂ ⁺	0.40	5×10^{15}	0.220	0.070	$2.50 \times 10^{20*}$	$6 \times 10^{20*}$	$6 \times 10^{18*}$	$1.5 \times 10^{20*}$
25-2	P ⁺	0.32	4×10^{13}	0.160	0.056	1.25×10^{18}	3×10^{18}	3×10^{16}	3.0×10^{16}
47-1	B ⁺	0.40	1×10^{14}	0.160	0.050	2.50×10^{18}	8×10^{18}	8×10^{16}	8.0×10^{13}

*Value for H⁺, assuming H₂⁺ dissociates during impact

peak, average, front and rear surface implant concentrations can then be calculated from the total dose by assuming a simple Gaussian profile for the projected range, i.e.

$$n(x_p) = \frac{\phi}{\sigma_p \sqrt{2\pi}} \exp \frac{(x_p - R_p)^2}{2\sigma_p^2}$$

where

- n = Volume concentration (cm^{-3})
- x_p = Depth at which peak concentration occurs (cm)
- ϕ = Total dose (ions cm^{-2})
- σ_p = Standard deviation in projected range (cm)
- R_p = Projected range (cm)

The B, P, and F implants proved to be straightforward. In the case of H, the optimum beam energy for H^+ implanted into $0.4 \mu\text{m}$ thick films is only 15 keV, below the useful energy range of commercial ion implantation systems. Consequently, it was decided to implant H_2^+ ions at 30 keV to achieve the same R_p . The concentration values in Table 1 are for H^+ , insofar as the H_2 will dissociate upon impact at such high energy.

The effects of ion implantation on a-Si properties have been evaluated by measuring the electrical conductivity as a function of temperature of a-Si films, before and after each implementation and after post-implant annealing treatment. Electrical contacts have been made by evaporating Au or Cr onto the film in a four-point configuration after each implant or anneal step. This procedure has been adopted in order to minimize effects due to contact metal diffusion into the implanted a-Si films.

Section 3

FILM CHARACTERIZATION

The as-deposited and the ion-implanted amorphous silicon films were characterized by several techniques in order to obtain quantitative and qualitative information on key parameters. The measurements included conductivity as a function of temperature, $\sigma(\tau)$, optical absorption as a function of energy, $\alpha(h\nu)$, the sign of the thermoelectric power, the sign and magnitude of the Hall effect, film thickness, infrared spectrum using Fourier Transform Infrared Spectroscopy (FTIR), and features of film morphology using transmission electron microscopy (TEM) and Raman Spectroscopy. The results of the measurements demonstrate that we are able to produce both a-Si and a-Si:H films which are controllably n- or p-type and that we can change the conductivity of these films after deposition by ion implantation.

Films deposited during the first quarter of this program were of four types:

- n-type amorphous silicon films without intentional hydrogen incorporation,
- p-type amorphous silicon films without intentional hydrogen incorporation,
- reactively sputtered n-type amorphous silicon films incorporating hydrogen,
- reactively sputtered p-type amorphous silicon films incorporating hydrogen.

The films were sputtered under various conditions of argon partial pressure, hydrogen partial pressure, and sputtering rate utilizing n-type single crystal silicon targets of 4×10^{16} As atom/cm³ and p-type targets of 3×10^{17} B atom/cm³ and 5×10^{18} B atoms/cm³. Substrates for the films included 7059 glass, quartz, sapphire, stainless steel, single crystal silicon and KBr. The films on 7059 glass and quartz were used primarily for conductivity measurements while the sapphire, KBr and single crystal silicon were used to make optical transmission samples. A number of films were deposited on gold-coated glass for easy removal as TEM samples.

3.1 ELECTRICAL CHARACTERIZATION

Figure 3 shows the conductivity as a function of temperature for 3 n-type amorphous silicon films and the room temperature conductivity for two other amorphous silicon films. No hydrogen was intentionally incorporated into any of these films. All films were sputtered from n-type single crystal silicon targets which were doped with 4×10^{16} As atoms/cm³. All films shown were sputtered with an argon partial pressure of approximately 2 mTorr. The parameter that was varied in the deposition of these films was the deposition power and hence the growth rate of the film. The deposition power was varied from approximately 250 W to 2 kW. The conductivity does not vary monotonically with the power; i. e. , films deposited at 1 kW and 2 kW are the high and low conductivity respectively, while the film deposited at 250 W is of intermediate conductivity. However, several deposition parameters in these experiments are not presently under control. A principal parameter for which control is being implemented is the substrate temperature. Although the depositions all began with the substrate at room temperature, the temperature at the end of the deposition varied considerably for each experiment. This parameter alone could account for the wide variation in conductivity.

Having described the anomalies in the data appearing in Fig. 3, the consistent features are all the more remarkable. It appears that all films show a thermally activated conduction process with a low-activation energy (0.135 eV for the high conductivity sample and 0.178 eV for the low-conductivity sample). The activation energy increases as the conductivity decreases. The sign of the thermoelectric power for all films is the same as that for an n-type semiconductor. The sign for the Hall coefficient measured on the highest conductivity film is also consistent with n-type semiconductors. The agreement between the sign of the Hall coefficient and the sign of the thermoelectric power for an amorphous semiconductor is an unexpected result. The amorphous nature of the high conductivity film in Fig. 3 was confirmed by x-ray diffraction and Raman spectroscopy.

Fig. 3 Conductivity Versus Temperature for N-Type a-Si Films Deposited at Several Film Growth Rates as Measured by Power in Plasma Discharge

Figure 4 shows the data for amorphous silicon films which were sputtered with a boron-doped p-type target. The description of the data is similar to the n-type films in Fig. 3. That is, all the films display thermally activated conductivity; they were deposited at different rates, and any conductivity dependence on deposition rate is indeterminate at this point. The p-type nature of these films was determined by measuring the sign of the thermoelectric power, and, in the case of the highest conductivity film in Fig. 4, the sign was consistent with the sign of the measured Hall coefficient. Raman spectroscopy confirmed that the high-conductivity film is amorphous.

In addition to the amorphous silicon films in which no hydrogen was intentionally introduced, films were prepared by reactively sputtering silicon with an argon-hydrogen gas mixture. The data from three separate experiments are shown in Fig. 5. All films were deposited at 1 kW power with an n-type target containing 4×10^{16} As atoms/cm³. The deposition parameter varied for the curves in Fig. 5 were the partial pressure of the hydrogen during sputtering, the argon pressure remaining constant. If the sputtering process is dominated by argon ion interactions at the target cathode, a constant argon pressure and constant power should yield a constant deposition rate. To first order, a constant deposition rate was observed. The relative hydrogen partial pressures for the three curves are 10 for the lowest-conductivity film, 6 for the highest-conductivity film, and 1 for the intermediate film. Optical absorption measurements showed a monotonically increasing optical gap width as the hydrogen partial pressure was increased. The appearance of the films themselves went from red-orange to yellow. As discussed in the F'IR data, the increase in hydrogen partial pressure seems to correspond to an increase in the ratio of Si-H₂ bonds over Si-H bonds.

Initial experiments involving the ion implantation of a-Si films were carried out this quarter. Figure 6 shows the conductivity versus temperature for several films implanted at room temperature with fluorine and hydrogen. These curves are for as-deposited and as-implanted films. Later these films will be annealed to study the activation of the implanted species. Both the hydrogen and the fluorine were

Fig. 4 Conductivity Versus Temperature for P-Type a-Si Films Deposited at Several Film Growth Rates as Measured by Power in Plasma Discharge

Fig. 5 Conductivity Versus Temperature for N-Type a-Si:H Films Reactively Sputtered in Various Hydrogen Gas Partial Pressures

Fig. 6 Conductivity Versus Temperature for N-Type a-Si Films Before and After F- and H-Implantation

implanted to average concentration levels of approximately $2.5 \times 10^{20} \text{ cm}^{-3}$. As seen in the figure, there is initially very little change occurring in the fluorine-implanted sample, while the hydrogen film shows a marked decrease in conductivity following implant.

Figure 7 shows the conductivity versus temperature results from an n-type a-Si film implanted at room temperature with phosphorous to average concentration levels of $1.25 \times 10^{18} \text{ cm}^{-3}$. It can be seen that the initial conductivity following implant has been significantly lowered while the activation energy has increased. Raising the temperature to 180°C to measure the conductivity represents a low-temperature annealing step. Figure 7 demonstrates that appreciable annealing of the implanted film occurs at even this low temperature in that the conductivity decreases and the activation energy increases for subsequent measurements made on film 25-2.

3.2 INFRARED SPECTRA

Infrared transmission spectra of a-Si and a-Si:H films sputtered onto sapphire substrates were recorded by means of a Fourier transform infrared (FTIR) spectrograph. The sapphire substrates are opaque at wavenumbers less than 1300 cm^{-1} , and, thus, only the Si-H_x stretch-mode absorptions in the $2000\text{--}2100$ wavenumber region could be observed. Such absorption structure did appear in the FTIR spectra of the hydrogenated samples as shown in Fig. 8. Sample #69 exhibits an absorption peak at 2020 cm^{-1} implying mostly Si-H bonding; that for sample #79 is centered at 2057 cm^{-1} implying existence of Si-H_2 bonding. The latter film was deposited with a hydrogen gas flow rate (and thus partial pressure) only 5 percent greater than the former, and it is surprising to see such a large shift for this small an H_2 pressure change.

Further work in this area includes a-Si:H reactive sputter depositions on crystalline silicon and KBr substrates over a greater range of H_2 flow rates. Thus, changes in the bend, bend scissors, wag and rock modes of the various Si-H_x incorporation structures can be observed. The immediate objective of these planar magnetron

Fig. 7 Conductivity Versus Temperature for N-Type a-Si Films Before and After P-Implantation

Fig. 8 Fourier Transform Infrared Spectra of $a\text{-Si:H}$ Films in the Si-H_x Stretch-Mode Region

experiments is to develop a simple model for H incorporation. This model will then be used to aid in determining the starting parameters for the upcoming series of cylindrical magnetron a-Si:H depositions.

3.3 TRANSMISSION ELECTRON MICROSCOPY

Several a-Si films were deposited on gold-coated glass substrates, where poor adhesion made it possible to obtain free-standing films for transmission electron microscope (TEM) analysis. A stereo-pair TEM photo of sample #14 (3300 Å thick) is shown in the top of Fig. 9. The granular structure, also seen by other investigators, is clearly visible. The dimension of the "grain" is on the order of 500 Å. Substructure of about 50 Å in size can be distinguished. There also appears to be a glaze covering the film — perhaps the surface oxide.

At the bottom left of Fig. 9 is an x-ray diffraction pattern for the film showing the broad ring image associated with amorphous films. (Subsequent Raman spectroscopy of similar samples confirmed the amorphous nature of the films.) The bottom center photo is a TEM image of the film taken during crystallization caused by local heating due to an increase in TEM beam current. The three crystallization tracks were seen to move from the lower right to the upper left in the field-of-view. The x-ray diffraction pattern for this partially crystallized film is shown in the bottom right. Both rings and spots are apparent. The multiple nature of the spots probably indicates a slight misorientation among crystals.

Photo Captions for Following Page

Fig. 9 Stereo Pair of Transmission Electron Micrograph (TEM) at 65000X of an a-Si 3000 Å Film; Lower Left Photo: X-Ray Diffraction Pattern of Amorphous Silicon; Center Photo: TEM of Crystallizing Amorphous Silicon Film; Lower Right Photo: Electron Diffraction Pattern of Film in Center Photo.

Section 4

PLANS FOR NEXT QUARTER

During the next quarter, the following activities are anticipated:

- (a) Continue deposition of a-Si:H films emphasizing cylindrical magnetron reactive sputtering by D. C. or R. F. sputtering of a CVD silicon target. Substrate temperature and H_2 partial pressure will be control parameters. Gas phase doping with PH_3 and/or B_2H_6 will be initiated. Sputter-deposited stainless-steel coated glass, crystalline Si, and KBr substrates will be included for various characterization needs.
- (b) Deposition of Schottky barrier devices using Pt and/or Au both in vacuo and after exposure to atmosphere.
- (c) Continue ion implantation studies in selected films to determine the effect of implant and/or anneal temperature on the electrical activation of H or F implants.
- (d) Continue electrical and optical characterizations such as:
 - Conductivity versus temperature in selected samples.
 - Optical and IR spectroscopy to determine optical absorption edge and alloying and impurity absorption structure (such as oxygen, nitrogen, etc.) in selected samples.
 - Hall mobility and/or thermoelectric power versus temperature to distinguish thermally activated carrier from mobility effects in high σ a-Si samples.
 - Field effect measurements to separate bulk from surface conduction mechanisms in low σ a-Si:H samples.
- (e) Continue structural characterization of selected films using TEM/SEM techniques.