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AMORPHOUS THIN FILMS FOR SOLAR CELL APPLICATIONS

Technical Progress Report for the Period October 11, 1980—January 15, 1981

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Section 1

INTRODUCTION

This Technical Progress Report reviews accomplishments of the program, "Amorphous Thin Films for Solar Cell Applications: a-Si by Magnetron Sputtering." Progress has been ahead of planned expectations in three instances, a) achievement of 4 mA/cm^2 , short circuit current density in a MIS structure solar cell under AM1 illumination, b) fabrication of large area (4 cm^2) MIS cells with external $J_{sc} > 3 \text{ mA/cm}^2$, and c) deposition of p^+ layers by B_2H_6 gas phase doping. A program status table is included as Appendix A. Reproducible n^+ layers are now routinely deposited by sputtering in Ar, H_2 , and PH_3 gases. The major remaining obstacle to the July 1981 goal of a 3.5% cell is the deposition of a quality i-layer. Although information deduced from infrared absorption and Raman data indicates that most of the hydrogen is bonded in the SiH configuration, the photoconductivity of the intrinsic material requires marked improvement.

Two forms of magnetron sputtering, planar and cylindrical, are being exploited to achieve program results. The planar deposition system has the advantage that experimental costs are low; the cylindrical system is easily scalable to large product throughput. The parallel approach of using two different magnetron systems brings an added dynamic aspect to the program as both similar and contrasting deposition results must be resolved. Schematic illustrations of the two systems and descriptions of apparatus modifications incorporated during this reporting period are included as Appendix B.

Section 2

N+ BACK CONTACT LAYER DEVELOPMENT

In order to develop an efficient solar cell, it is necessary to limit the back contact resistance to well below 1 ohm-cm^2 . Ohmic contact must be made with the highly resistive intrinsic layer. This contact can be achieved by preparing a highly doped n^+ contact layer with the use of reactive gas-phase doping. We began the development of such a layer using a mixture of Ar and PH_3 (0.3%) gas and H_2 gas in the planar magnetron system. Films were prepared at a partial pressure of 1.5 mtorr argon or argon plus phosphine while the partial pressure of H_2 was varied from 0.05 to 0.50 mtorr. Reproducible high conductivity films were routinely prepared when the PH_3 in the Ar was increased to 3% for $P_{\text{Ar}+\text{PH}_3} = 4$ and 8 mtorr. The substrate temperature was 370°C . Figure 1 summarizes these results. It is observed that as P_{PH_3} is increased, room temperature conductivity (RTC) increases to an asymptotic value slightly greater than $10^{-2} \Omega^{-1} \text{ cm}^{-1}$. The deposition parameters which yielded this value were perturbed in order to check the influence of deposition rate and substrate temperature on the RTC. These results are shown in the inset of Fig. 1. Decreasing substrate temperature from 370° to 200°C resulted in a factor of 5 decrease in RTC. Increasing deposition rate from 170 to 500 $\text{\AA}/\text{min}$ resulted in a factor of 10 decrease in RTC. The latter result indicates a reduction in dopant incorporation as the PH_3/Si flow rate ratio (at the substrate) is reduced; the former result might indicate reduced dopant activation as well as reduction in dopant incorporation.

Figure 2 shows the n^+ layer deposition results for the cylindrical system at the gas pressures, $P_{\text{Ar}} = 1.5$ and $P_{\text{H}_2} = 0.5$ mtorr, chosen from extrapolation of i-layer material conditions. The PH_3 flow rates varied from 0.1 to 3.7 SCCm making the PH_3/Si flow rate ratio overlap several values used in the planar n^+ deposition. Note that the highest RTC value is comparable to that in Fig. 1 and occurs at about the same substrate temperature, 350° vs 370°C . Temperature

Fig. 1 Planar Magnetron N^+ Film Deposition Parameters Versus Room Temperature Conductivity

Fig. 2 Cylindrical Magnetron N^+ Film Deposition Parameters Versus Room Temperature Resistivity

decrease from 350° to 200°C resulted in a factor of 10 decrease in RTC. This is more precipitous than that shown for the planar samples in the inset of Fig. 1. Such a difference might be expected in that the latter samples are sputtered in a partial pressure of H_2 given solely by the PH_3 dissociation. There are also slight deposition rate differences between results in Figs. 1 and 2.

In order to more closely compare the RTC results among the two magnetron sputtering geometries and the glow discharge method, refer to Fig. 3. Here the PH_3 doping curve is determined from Spear (Ref. 1) assuming 100% decomposition of SiH_4 . The cylindrical curve was determined from measured PH_3 flow rates, while the planar curve was determined from measured PH_3 partial pressures converted to flow rates via known pumping speeds. The Si flow rate was computed from measured Si deposition rate profiles at known cathode currents in both cases.

First, it appears that the Spear curve can be superimposed on the cylindrical results if rather than 100%, a 10 – 20% SiH_4 decomposition is assumed. Next, the planar curve can also be superimposed when differences in ion flux given by cathode current and sputtering yield given by operating voltage are accounted for in both sputtering machines. The ion flux ratio (2 A in cylindrical, 0.2A in planar) moves the planar curve 1 decade and the sputtering yield ratio (at 850 V in cylindrical, 200 V in planar) moves it by a factor of 3 for a total factor of 30 to the left. (Ref. 2)

With the $10^2 \Omega\text{-cm}$ material, one is able to deposit 250 Å thick back contacts with resistance of $2.5 \times 10^{-4} \text{ ohm -cm}^2$. This is of the same order as typical contact resistances and the total back contact resistance is within desired limits.

Fig. 3 Phosphine Gas Phase Doping for N^+ Contact Layer: Comparison of Room Temperature Resistivities Among Silane Decomposition and Planar and Cylindrical Magnetron Sputtering Deposition Methods.

Section 3

INTRINSIC LAYER DEVELOPMENT

In both the MIS test-structure solar cell and the PIN configuration for the most promising cells, limitations in the photoelectronic properties of the i-layer will severely hamper photovoltaic performance. Recognizing that the best test of the i-layer quality will be in the measure of its device behavior, one is tempted to perform MIS cell fabrications throughout a wide range of deposition parameter space. However it is evident that a series of constraints must be imposed on this approach, for the deposition space is at least 6-dimensional: these dimensions include substrate temperature, partial pressures of argon and hydrogen, deposition rate, substrate surface condition and distance to target. After dimensional constraints to this space are determined (more later), starting values and the mesh size for the discrete search must also be chosen.

Our approach has been to screen candidate device quality materials by first obtaining reproducible optical and electronic properties of separate i-layer depositions and then to incorporate the best films into device fabrications. We have chosen to measure, a) the optical absorption in order to determine the optical band gap (Ref. 3), b) the film conductivity and photoconductivity as a gauge of the efficiency of hydrogenation on decreasing density of states in the gap, and c) the infrared absorption (or Raman Scattering) to model the Si-H bonding arrangements. Selected films are measured for impurity content; others are investigated for growth morphology.

As mentioned above, the complexity of the deposition space must be simplified. Substrate temperature and argon and hydrogen partial pressures are chosen as the first order deposition variables. Deposition rate, substrate surface and distance to target are reserved as secondary variables. That is, they are held constant unless specific questions arising from primary results require their being perturbed. Plasma location with respect to substrate and substrate bias

are additional control parameters in both the planar and cylindrical systems. These have been held constant.

The i-layer film efforts during this reporting period have concentrated on investigating the low hydrogen partial pressure regime of the deposition space. The study was motivated in this direction because some of the better glow discharge produced cells of RCA contained less than 10% hydrogen, while our earlier i-layers contained up to twice this amount (Ref. 4). Of course, there is no a priori knowledge to indicate existence of a direct correspondence between glow discharge and magnetron sputtered material properties. In fact, recent information from Exxon's diode sputtering work (Ref. 5) indicates that gap density of states is beneficially reduced (from a device point-of-view) at high hydrogen content in the i-layer film.

Optical measurements shown in Fig. 4 are summarized as follows. First, the optical gap as expressed by E_{04} increases with P_{H_2} . Second, there is good agreement on E_{04} values between planar and cylindrical films deposited at reduced hydrogen partial pressures ($0.1 < P_{H_2} < 0.5$ mtorr). Third, the relation between E_{04} and P_{Ar} is not monotonic for the series of films made at $P_{H_2} = 0.25$ mtorr. However, the general trend for all except the lowest P_{H_2} films is that E_{04} decreases as P_{Ar} increases. It is perhaps not coincidental that over this range of argon partial pressures the gas collision mean free path becomes comparable to substrate-target distances. Thus it can be agreed that molecular collisions play a role in the film deposition process; that is, either that dihydride formation becomes favored subsequent to a [Si, Ar] or [Si, H] gas-phase collision event, or the lower density film itself encourages growth of dihydride phase. It is known that at high P_{Ar} both film stress and argon incorporation are reduced, (Ref. 6) probably due to the increase in [Ar, Ar] gas-phase collisions. Perhaps the reduction in energetic argon bombardment aids in the formation of the dihydride as a second phase in the growing film. Thus, the decrease in E_{04} with increased P_{Ar} could simply imply the formation of two-phase material.

It should be mentioned that the magnetron machine is ideally suited to take advantage of benefits in low pressure deposition while maintaining separate control over any deleterious effects of plasma-substrate interactions.

Fig. 4 Energy Gap E_{04} Versus Hydrogen Partial Pressure
For a - Si: H Films
Magnetron-Sputtered at Various Argon Partial Pressures

Section 4

DEVICE DEVELOPMENT

The purpose of this task is to determine the capability of magnetron sputtering for producing device grade intrinsic (i) a-Si:H material using an MIS solar cell structure as a diagnostic tool. Progress to date includes a large area cell ($> 4 \text{ cm}^2$) with measured short circuit current density $> 3 \text{ mA/cm}^2$.

During this reporting period, these devices were constructed as follows. First, 150-200 nm of stainless steel was sputter-deposited into a 1 in. x 1 in. 7059 glass substrate. Next, 28 nm of n^+ material (see Section 2) was deposited for back surface ohmic contact, followed by 300 to 700 nm of i-layer deposited at $T_S = 250$, $P_{Ar} = 1.5$ and $P_{H_2} = 0.5$ mtorr. Next, on selected samples, 3.6 nm of Pt was deposited as the $\sim 50\%$ transparent Schottky barrier layer. Other samples were removed from the sputter chamber for subsequent evaporation of 50% transmitting Au or Pd Schottky barrier layers. Finally an In grid was evaporated on top of the barrier layer to facilitate the current collection. Active areas varied from 0.017 cm^2 to $> 4.0 \text{ cm}^2$.

4.1 SMALL AREA CELLS

Figure 5 shows the dark and AM1 current-voltage characteristic of one of the thirty small area (0.017 cm^2) cells fabricated on device D715. For most of these cells, the open circuit voltage (V_{oc}) varied between 0.38 and 0.40 volts; short circuit current density (J_{sc}) varied between 2.7 and 3.1 mA/cm^2 . Fill factors (ff) were approximately 0.30. The remainder of the cells were found to be shorted.

Similar results were found for other Pd cells and for those fabricated using Au or Pt Schottky barriers. A question concerning the low V_{oc} value arose. Was this limited by the barrier height or do surface states pin the value at 0.4 volts?

Fig. 5 Current Voltage Characteristic for Pd MIS Solar Cell D715

In order to answer this question, neutral density filters were used to measure I_{sc} versus V_{oc} for a series of temperatures between -97 and 131°C as shown in Figure 6.

The theoretical waves were plotted using shunt conductance $G = 1.45 \times 10^{-7} \Omega^{-1}$ which was the measured value. The ϕ_B and I_{oo} values were deduced from the data assuming an ideality factor (n) equal to unity. The solid curves show the match between theoretical calculations with the four fitting parameters G , ϕ_B , I_{oo} , n , and the measured V_{oc} , I_{sc} points. Actual ideality factor was measured with a correlation coefficient of 0.9978 to be closer to 1.044 when fitted to V_{oc} , I_{sc} data points at room temperature. The resulting barrier height of 0.979 volts indicates that the i-layer surface state density is responsible for pinning the AM1 value of V_{oc} at 0.4 volts.

One device (#591) containing 50% transmitting Au Schottky small area cells achieved a J_{sc} of 4 mA/cm^2 . This cell was actually a photodiode in series with a tunnel diode as determined from its I-V characteristic. This cell structure might have been the result of inadvertent exposure to H_2O immediately subsequent to its fabrication.

4.2 LARGE AREA CELL

Efforts to solve the pinhole problem mentioned above had progressed far enough (as indicated by a reduction in number of shorts on the small area cells) to attempt a large area cell deposition.

Figure 7 shows the current-voltage characteristic (and the $I \times V$ product curve) for a Pt Schottky barrier cell fabricated with an area of approximately 4 cm^2 . The open circuit voltage was again pinned at 0.4 volts while the short circuit density of 3 mA/cm^2 (45% transmitting Pt) is no worse than that achieved in the small area cells. The fill factor is ~ 0.35 . There is no AR coating and the grid is approximately 9% of the 4 cm^2 area.

Fig. 6 Short-Circuit Current vs Open Circuit Voltage for Cell D715

Fig. 7 Current Voltage Characteristic for Large Area Pt MIS Solar Cell No. D774

Figure 8 depicts the relative spectral response curve for this large cell #D774. The E_{04} optical gap, measured on a separate i-layer monitor film deposited at the same conditions as the device i-layer, is also shown. The long wavelength response increased is caused by optical interference effects.

That the large area cell shows no performance degradation compared to the small area cells is encouraging. This indicates that there is considerable room for improvement in the cell performance of these materials.

4.3 PIN CELLS

Work on PIN structure cells began during this reporting period. Diborane gas-phase doping depositions were successful in producing p^+ layers with conductivity of $5 \times 10^{-3} (\Omega\text{-cm})^{-1}$. To date, the PIN structures deposited are used only to determine cross-contamination effects between adjacent layers.

Fig. 8 Spectral Response for Large Area (4 cm^2) Cell D774 - Pt MIS.
 E_{04} is Measured for i-Layer Material Deposited on 7059 Glass.

Section 5
REFERENCES

1. Spear, W. E., Adv. in Physics 26, 811, 1977.
2. Blank, P. and Wittmaack, K., J. Appl. Phys. 50, 1519-28, 1979.
3. D. E. Carlson, private communication.
4. This was estimated from Raman measurements made by R. Nemawich at Xerox Palo Alto Research Center.
5. T. D. Moustakas, Amorphous Silicon/Materials Subcontractors' Review Meeting, Denver, Colo., Feb. 9-11, 1981.
6. J. Thornton and D. Hoffman, "Internal Stresses in Amorphous Silicon Films Deposited by Cylindrical Magnetron Sputtering Using Ne, Ar, Kr, Xe, and Ar + H₂" presented at the 27th National Symposium of the American Vacuum Society, Oct. 13-17, 1980, Detroit, MI.

Appendix A

PROGRAM STATUS

The program milestones and status to date are included in Table A-1. The table shows at a glance that all program milestones are either partially or fully achieved, some ahead of schedule.

Table A-1 PROGRAM MILESTONES

PLAN		STATUS
1ST QUARTER (OCT 1980)	USABLE N^+ BACK CONTACT LAYER DEMONSTRATED	▲ RELIABLY REPRODUCED N^+ LAYERS DEPOSITED IN BOTH PM & CM SYSTEMS USING PH_3 GAS-PHASE DOPING
2ND QUARTER (JAN 1981)	i-LAYER PARAMETER SPACE PLOT OBTAINED	▲ MAPPING OF PARAMETER SPACE TO OBTAIN HIGH PHOTOCONDUCTIVITY i-LAYER CONTINUES
3RD QUARTER (APR 1981)	SOLAR CELL DEVICE: $J_{SC} > 4 \text{ ma/cm}^2$ $\eta(\text{AM1}) > 2\%$	▲ M-i-s STRUCTURE SOLAR CELLS DEPOSITED WITH MEASURED $J_{SC}(\text{AM 1}) > 4 \text{ ma/cm}^2$ (55-60% TRANSMISSIVE Au OR Pd SCHOTTKY BARRIERS)
4TH QUARTER (JULY 1981)	SOLAR CELL 1 cm^2 : $\eta(\text{AM1}) > 3.5\%$	▲
ADDED ITEM		▲ P^+ LAYERS DEPOSITED IN PM SYSTEM USING B_2H_6 GAS-PHASE DOPING

Appendix B

APPARATUS MODIFICATIONS

B.1 PLANAR SYSTEM (LMSC)

- A) The planar magnetron system shown in Table B-1 has been upgraded to accomodate separate B_2H_6 and PH_3 gas lines to the reactive gas manifold. This eliminates the exceedingly long gas line pumpdown required between P and n layer depositions when a single doping gas line was used.
- B) Both dc and rf bias voltages can now be applied to the substrate platform.
- C) A graphite heater has been installed in order that substrate temperatures up to 400° C be achievable.

B.2 CYLINDRICAL SYSTEM (TELIC)

A schematic diagram of the cylindrical system is shown in Table B-2. The advantage of this geometry for production level throughput is evident when one considers the substrate area accommodated per deposition.

The cylindrical cathode is subjected to heating during sputtering and must be cooled. During this reporting period, a closed cycle, de-ionized water, cathode cooling system has been installed. It is connected through a tubular counter-flow heat exchanger to the city water system and provides a controlled 0.3 gpm flow of water through the cathode. The cooling water reaches a temperature of 115°F at the standard 2 kW operating condition that has been used in our previous α -Si deposition runs. The closed cycle system has the advantages that clean water is passed through the cathode and that only a limited and controlled amount of clean water would pass into the vacuum system in the event of a cathode failure.

Fig. B-1 LMSC Planar Magnetron Sputtering System

Fig. E-2 Cylindrical-Post Magnetron Reactive Sputtering System Schematic