MASTER

DOE/ET/23038-3

Distribution Category UC-63e

BLACK a-Si:H SPUTTERED FILMS FOR PHOTOVOLTAIC SOLAR CELLS

Quarterly Technical Progress Report No. 3
November 16, 1979 - February 15, 1980

R. Messier, I.S.T. Tsong, Principal Investigators

The Pennsylvania State University
Materials Research Laboratory
University Park, PA 16802

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for the U.S. Department of Energy,
Division of Solar Energy, Photovoltaic Programs Office
UNDER CONTRACT NO. DE-AC03-79ET23038

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

Introduction	1
Results and Discussion	1
Deposition Rate	2
Density	2
Internal Stress	2
High Energy Ion Beam Annealing Effects	5
References	9

INTRODUCTION

Background information on sputtered a-Si:H films in general and our approaches to this area of research in particular have been discussed in our two previous quarterly reports and will not be discussed further here. During this third quarter our effort has been directed toward the characterization of a series of thin films prepared during the first half of this contract in which the primary variable parameters are the total gas pressure (Ar + H₂ as expressed in mTorr) and partial pressure of hydrogen (as expressed as a percentage of the total gas pressure). This comprehensive characterization of the structure, composition and properties has included the following:

- microstructure and nanostructure
- composition (Si, Ar, O, H)
- deposition rate
- density
- internal stress
- optical absorption
- substrate self-bias voltage

Even though work was carried out on all of these areas, we report here only on the deposition rate, density, and internal stress measurements and on high energy ion beam annealing effects. We leave the remainder, which were still in progress, for complete presentation and discussion during the last quarter.

RESULTS AND DISCUSSION

Deposition Rate: Deposition rate was calculated from the total time for deposition and film thickness measured at steps created by ~100 μ m-thick masking glass coverslips. Step height was measured with a Taylor-Hobson Talysurf 10 stylus profilometer. Deposition rate was calculated at 1cm

intervals radially to a distance of 7cm; an average deposition rate was calculated from the three interior rates.

Film thicknesses necessary for calculations in other measurements were taken at steps made by a particular substrate where possible, and otherwise were calculated from substrate position and deposition rate as a function of radial distance.

For vertical displacements on the order of the film thicknesses studied ($\sim 10\mu\text{m}$) both the accuracy and precision of the calibrated profilometer measurements, and thus deposition rate, are within 5%. The deposition rate as a function of P_T and %H is given in Figure 1. In general, the deposition rate increases with P_T , reaches a maximum at $P_R \approx 20\text{mTorr}$, and decreases thereafter. The deposition rate, generally decreases with increasing %H, although the effect for small %H is not as straightforward because of other factors, to be discussed later.

Density: Film Density was estimated from film mass; as calculated from the difference in substrate/substrate-film mass, and film volume, as estimated from substrate area and film thickness. A systematic error in the calculated density can be introduced by film growth on the substrate edges; we judge this to be a maximum of +5% in our case and superimposed on this is a random effort of $\sim \pm 5\%$, as indicated by data spread.

Figure 2 shows the dependence of film density upon P_T and %H for $P_T = 40$ and 70mTorr. It is indicated that films prepared without H at those pressures are near the density of c-Si ($\rho = 2.33\text{gcm}^{-3}$), but that the introduction of hydrogen yields low density films, with about 75% of the density of c-Si. Similar results have been reported by others.

Internal Stress: Macroscopic stress in the films was calculated by Stoney's technique⁽¹⁾ as elaborated by Brenner⁽²⁾.

Figure 1 Deposition rate as a function of sputtering gas pressure.

Figure 2 Density of high P_T films as a function of %H.

For films on a substrate free to deform continuously during film deposition,

$$S = \frac{Et(t+d)}{6rd}$$

where S = stress at the film surface, E = Young's Modulus of substrate, t = substrate thickness, d = film thickness and r = radius of substrate curvature,

The stress in the film at a distance x from the film substrate interface is given by

$$S(x) = S \left(1 + \ln \frac{t+x}{t+d} - \frac{3(t-d+2x)(d-x)}{(t+d)(t+x)} \right)$$

Our measurements were made for films on thin ($\sim 150\mu\text{m}$) glass coverslips with E estimated as 6.9×10^{11} dynes cm^{-2} (3). We obtained r from the film-substrate system deflection measured with a Talysurf 10 profilometer.

Figure 3 shows the variation of internal stress with P_T and %H. We observed stresses as high as $\sim 4 \times 10^9$ dyne cm^{-2} for $5\mu(0\%H)$. Compressive stress decreases fairly regularly with increasing P_T and increasing %H, and obtains an approximately nil value for films prepared at the highest P_T and %H.

HIGH ENERGY ION-BEAM ANNEALING EFFECTS

Staebler⁽⁴⁾ has described the irreversible darkening of room-temperature-deposited glow discharge (GD) a-Si:H films upon exposure to a focused laser beam. He attributed this effect to thermal annealing which causes evolution of H_2 , increase in film oxygen content, and general atomic rearrangement, although without recrystallizing action.

We report similar behavior resulting from exposure to $\sim 17\text{MeV } ^{19}\text{F}^{47}$ in sputter-deposited (SD) a-Si:H films prepared at high P_T (and containing H predominantly as di hydride).

Figure 3 Intrinsic stress vs. %H for various P_T .

Figure 4 shows SEM micrographs of a beam-affected region in a sample prepared at $P_T = 40\text{mTorr}$ and 10%H in the plasma. Nuclear reaction measurements indicate ~ 30 at %H in this film, although the depth profile was erratic due to H migration and evolution. IR spectral measurements show dihydride bonding exclusively, and microprobe measurements indicate $\sim 0.1\text{wt\% Ar}$ and $\sim 5\text{wt\% O}$. The film was $\sim 5\mu\text{m}$ thick, was light reddish in appearance preceeding exposure (with an optical bandgap of $\sim 2.0\text{eV}$) and darkened to the extent of becoming opaque after exposure.

We observe the same effect for all SD a-Si:H films with high dihydride content that have been examined with $^{19}\text{F}^{47}$ with $120\text{-}2500\text{nA/cm}^2$ and approximately equal exposure times of ~ 5 minutes. The effect is not observed in SD a-Si (w/o H) nor in SD a-Si:H in which monohydride predominates. Our evidence indicates that SD a-Si:H films which exhibit the darkening behavior are similar to the GD a-Si:H films described by Staebler and that the mechanism of darkening is essentially the same for the high energy ion beam as for the laser beam. We get good correspondence in our H-determination by IR and nuclear reaction analysis only for the films which do not degrade under beam irradiation.

Figure 4 SEM micrographs of SD a-Si:H irradiated by 17MeV $^{19}\text{F}^{47}$ showing (a) micron sized patches resulting from film shrinkage with H_2 evolution and (b) columnar nature of the film [magnified image from central portion of (a)].

REFERENCES

1. G. G. Stoney, Proc. Roy. Soc. (London) A 82, 172 (1909)
2. A. Brenner and S. Senderoff, J. Research of NBS 42, 105 (1949).
3. Handbook of Materials Properties.
4. D. L. Staebler, J. Appl. Phys. 50 (5), 3648 (1979).