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BLACK a-Si:H SPUTTERED FILMS FOR PHOTOVOLTAIC SOLAR CELLS
Final Technical Progress Report for the Period May 15, 1979—May 15, 1980

By
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I. S. T. Tsong

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The Pennsylvania State University
Materials Research Laboratory
University Park, Pennsylvania

U.S. Department of Energy

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FINAL REPORT

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

Final Technical Progress Report

May 15, 1979 - May 15, 1980

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ABSTRACT

Relative to glow discharge (GD) produced a-Si:H films, sputter-deposited (SD) films have received less attention and have proved less useful in multi-layer thin film solar cells for a variety of reasons including (1) general film instability with respect to post-deposition oxidation/degradation, (2) difficulty in controlling Si:H bonding configuration, and (3) poor conversion efficiency: best reported values to date are GD $\approx$ 7%, SD $\approx$ 2%. Thus, as a first step in attempting to understand the many interrelated deposition processes and film characteristics which govern SD a-Si:H film "quality", we have examined in detail a number of important basic film characteristics as a function of the preparation parameters total plasma pressure P_T and H_2 partial pressure, %H (in Ar), for the range $P_T = 5\text{--}70\text{mTorr}$ and %H = 0.10. We have systematically prepared a series of films in this region of deposition parameter space and have characterized these films with respect to surface and internal microstructure, chemical reactivity and etchability, total elemental composition, H-bonding configuration, intrinsic mechanical stress, optical bandgap, and mean density.

In general terms, the films are described by a transition of properties dependent upon both P_T and %H. Films prepared at high P_T display a distinct columnar morphology with varying extent of intercolumn void or low-density regions. Some of these films have densities as low as $\sim 60\%$ that of c-Si, contain H predominantly in the dihydride bonding configuration, and undergo post-deposition oxidation to an extent as great as $\sim 10\text{wt}\%$. Films prepared in the low P_T regime are without detectable microstructure and chemically stable with no detectable bulk oxidation after many months. In these films we find up to 20 at%H almost entirely as monohydride, Ar content as high as 7 at%H, and compressive intrinsic stresses as large as $5 \times 10^9 \text{ dynes/cm}^2$.

These results are entirely consistent with the general Structure Zone Model (SZM) of physical vapor deposition upon which there are superimposed the "chemical" effects of H_2 reactive sputtering.

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

The Effects of Total Plasma Pressure and H₂/Ar Pressures in Controlling the Properties of RF Sputtered a-Si:H Thin Films for Photovoltaic Application

I. INTRODUCTION

The background information on a-Si:H films and their potential for solar cell devices has been described previously by us⁽¹⁾ and others⁽²⁾ and needs no further discussion. Currently, the preferred method of preparation of these materials is by the glow discharge decomposition of silane plus appropriate dilutant and dopant gases and, accordingly, has been studied most extensively⁽³⁾. This general preparation method has a number of variations (eg. rf, dc, bias, capacitive, inductive) with each one having a wide range of deposition variables (eg. substrate temperature, gas pressure, flow rate, gas composition, power level, anode, cathode, anode-cathode spacing) and resulting range of film properties. Again, we will not discuss this set of literature directly, though some of it will come into discussion as it relates to the common problems between the glow discharge and sputtering methods of preparation of a-Si:H films. In the rest of this introduction, we will review the current status of the reported literature on the sputter-deposition of a-Si:H, the questions it has answered, questions raised, and critical questions remaining. Finally, we will discuss our research between our initial proposal and the start of our current contract as it applies to our research approaches. The significant results to date on our current contract are presented in Section II.

A. REVIEW OF rf-SPUTTERED a-Si:H FILMS

By far the most extensive work reported on hydrogenated a-Si sputtered films has been by the Harvard group. Recognizing the importance of sample preparation conditions on resulting film structure and electronic properties, they have chosen to vary the partial pressure of Ar ($P_{Ar} = 5 - 50\text{mTorr}$), partial pressure of H₂ ($P_H = 0 - 5\text{mTorr}$), and substrate heater temperature (25 to 450°C) while keeping other parameters constant such as rf-power level (1.6 W/cm², 1.5kV) and substrate-target spacing (7cm). Through a series of papers⁽⁴⁻¹³⁾ they have attempted to gain a basic understanding of the critical relations between preparation, film structure, electronic properties, and device properties by studying a set of samples prepared within their limited (necessarily) preparation-parameter-space.

Pawlewicz⁽¹⁴⁾ (Battelle Northwest) studied the variation in properties of a-Si films as a function of Ar gas pressure (10 to 150mTorr), substrate heater temperature (25 to 450°C) and substrate-target spacing (2 to 12.5cm) with only one test reported on hydrogenated a-Si (Ar = 3% H₂ at 150mTorr). Moustakas (now at Exxon) is actively working on rf-sputtering of a-Si:H but has not published any results other than a recent review article⁽¹⁵⁾. McMillan and Peterson (Argonne National Laboratories) have studied both glow discharge and rf-sputtered material by thermal decomposition and IR studies⁽¹⁶⁾. Brodsky, Cardona, and Cuomo⁽¹⁷⁾ have made a detailed vibrational spectroscopic analysis of several samples prepared by glow-discharge and rf-sputtering. For the latter method, only one film was studied which was prepared at 1.7kV target voltage, substrate heater temperature of 200°C, total gas pressure of 20mTorr Ar + 10% H₂, and -50V rf-bias on the substrate. In a related study, Bermejo and Cardona⁽¹⁸⁾ have investigated the Raman scattering in an additional three samples. Finally, although the RCA group has studied rf-sputtered a-Si:H films, they have not yet published their results in the open literature.

From the above summary of the reported literature of the preparation and characterization of a-Si:H films by rf-sputtering, it is clear that only a limited range of preparation variables have been studied even though the resulting physical properties cover a very wide range. As in the glow-discharge method, the plasma in the rf-sputtering process is complex and highly dependent on all the preparation parameters including system geometry and even the coatings on the wall of the system. Thus, optimum conditions established in one system will not necessarily be the same as that in any other system. In order to fully understand a sputtered thin film material, then, it is necessary to establish the complex preparation-structure-composition-property relations.

Knights et al.⁽¹⁹⁻²⁹⁾ have studied in some detail these relations for glow-discharge prepared a-Si:H films. Especially in the area of the structure and microstructure of these materials they have made significant contributions which have led to a model of the a-Si:H structures comprising this class of materials. By combining their IR, Raman, SEM, TEM, hydrogen concentration and evolution studies they have established a picture in which ~100Å diameter columns of more or less intrinsic a-Si (perhaps with point defects of monohydride substituting for Si) are nucleated at the substrate interface and grow in the direction of the impinging vapor stream, the individual columns being separated by lower density regions. Such regions, they suggest, are comprised of polysilane chains, (SiH₂)_n.

along with monohydride saturation of the dangling bonds. For "good" material, these low density regions are minimal and thus monohydride arrangements are predominant. Also, such materials are more resistant to post-deposition oxidation and show no noticeable microstructure at the $\sim 1000\text{\AA}$ level though the $\sim 100\text{\AA}$ columns are still present. In turn, they have used this knowledge as a basis for better understanding the resulting physical properties which are of direct interest to device applications.

The structure and microstructure of a-Si:H sputtered films, however, has not been studied except, indirectly, by IR and Raman spectroscopy^(4,5,17,18). Although void, or low density, network structures similar to those found for glow-discharge a-Si:H have been shown for pure a-Si and a-Ge films they have not yet been confirmed for sputtered a-Si:H⁽²²⁾. Recently, we have shown by atom probe field ion microscopy (APFIM)^(30,31) and etching studies⁽³²⁻³⁴⁾ that similar void networks exist in a-Ge:H and a-Si:H and will be discussed more below.

Approaches to understanding the relation between preparation conditions and resulting film structure and properties have mainly centered on bombardment processes occurring at the growing film surface^(4,14,22) and the stability of molecular species both in the gas phase and on the film surface⁽²²⁾. For sputtered films only bombardment processes have been considered, the general idea being that it produces defect centers which cannot be significantly reduced in order to minimize gap states, except possibly by thermal reorganization. Although both Anderson, et al.⁽⁴⁾ and Pawlewicz⁽¹⁴⁾ come to this same conclusion based upon their sets of systematically prepared and characterized samples, they differ in their proposed mechanisms for bombardment reduction. Pawlewicz suggests that low-defect-density films occur only at high gas pressures (150mTorr) due to thermalization of energetic particles while Anderson, et al. suggest that film damage is due primarily to incident Si atoms and that these are thermalized at much lower gas pressure ($> 10\text{mTorr}$). We have recently found (see 2nd Quarterly Report) that significant amounts of hydrogen are included in a-Si films prepared in pure Ar at high pressures which would cast some doubt on the conclusions of Pawlewicz. Also, we have shown that significant thermalization of high energy particles occurs only at very high gas pressures ($> 200\text{mTorr}$)⁽³⁵⁾. However, high negative self-bias voltages ($> 20\text{V}$) are known to occur especially at low gas pressures ($< 25\text{mTorr}$) which can lead to significant positive-ion-bombardment, and even re-sputtering, effects⁽³⁶⁾. Although, clearly, more work is needed to understand this effect, it does appear that it will require a delicate balance between bombardment effects, thermal annealing effects during deposition, and

possibly other effects in order to make sputtered films with the same good characteristics as glow-discharge films. Our new results on the preparation of sputtered films with a very high monohydride/dihydride ratio is the first such report (see Section III B) and indicates we may be close to achieving this balance.

The chemical characterization of a-Si:H films has been based, to date, mainly on interpretation of the IR transmission data^(4,5,7,37). Further, most work has been on the quantification of the H-content, with the methods of SIMS⁽³⁸⁾ nuclear reactions⁽³⁹⁾ and hydrogen evolution^(16,40) used in some cases. But H-content data by itself has only limited significance since it does not uniquely define the structure⁽²¹⁾. Information such as the distribution of H and its bonding configurations within the structure are what is needed⁽²²⁾. No direct determination of oxygen content has been reported though Freeman and Paul have attempted an indirect determination from their IR spectra⁽⁵⁾. For sputtered films, only Pawlewicz has measured Ar-content of a-Si sputtered in pure Ar⁽¹⁴⁾. Since rather high amounts of Ar can be included in sputtered films (we have recently measured amounts as high as ~4 at % Ar), the alloying effect of this element could have a significant, though yet unidentified, effect on physical properties. Thus, a real material must be considered an a-Si:H:O:Ar alloy.

The complex relations of these many preparation and materials factors and their synergistic effect on physical properties of a-Si:H sputtered films is established but not well understood. Anderson, Moddel, and Paul⁽¹³⁾ have just reviewed the further relations between physical properties and Schottky barrier solar cell performance for sputtered a-Si:H and have concluded that no one property measurement by itself can predict device performance but, taken as a whole, can indicate directions for device optimization. They further conclude that "It is becoming increasingly clear that these two deposition processes (glow-discharge and sputtering) can produce films of similar quality." Despite this optimism, it is clear that much more work will be required before optimum and reliable devices are obtained by the rf-sputter deposition method.

B. OUR PREVIOUS RELATED RESEARCH

During the period between the submission of our original proposal and the start of our current contract, we have carried out research germane to our present and future research objectives and thus will be outlined here. In a series of papers⁽³⁰⁻³³⁾, we have addressed the questions of the preparation, chemical characterization, and microstructure of a-Si, a-Ge,

and a-Ge:H rf-sputtered films. The important points of these studies are listed below.

- 1) We have developed a new thin film characterization technique, atom probe field ion microscopy (APFIM), which allows, for the first time, a direct view of the three-dimensional atomic structure of a thin film in both the nucleation and growth stages plus a chemical analysis of vapor species field evaporated during the depth profiling process⁽³⁰⁾. The presence of a high percentage of clusters in a material has been confirmed for the first time. By this technique, we have studied materials ranging from insulators to semiconductors to metals.
- 2) In a detailed study of voids in a-Ge and a-Ge:H sputtered films⁽³¹⁾ we showed that the void networks are really low density regions which surround $\sim 100\text{\AA}$ diameter columns, are aligned in the direction of the impinging vapors, and originate at the film/substrate interface. This interface is not distinct but graded over $\sim 10\text{-}30\text{\AA}$ indicating some type of mixing (probably bombardment-induced). Further, the column size does not appear to change with film thickness.
- 3) The anisotropic etching behavior of a-Ge sputtered films has been studied extensively^(32,33). In addition to their application to photo-thermal energy conversion, our research has shown that the etching behavior reveals the microstructure of both the void and macrovoid networks present in these materials. A third type of void (microvoids) which surrounds the $100\text{\AA}$ diameter columns is not revealed by etching and can only be viewed by TEM or FIM. The three types of voids can be classified by the Structure Zone Model⁽⁴¹⁾ developed primarily for crystalline metal films and thus provides a way of comparing the microstructure of amorphous semiconductor films prepared by different laboratories or different processes.

C. WORK ACCOMPLISHED DURING FIRST THREE QUARTERS

The details of work reported during the first three quarters of this contract will not be repeated in this report though some of these results are summarized and discussed here. The reader is referred to these reports for details on film preparation (1 and 2), etching behavior and microstructure (1 and 2), IR spectroscopy (2), hydrogen analysis (2 and 3), and deposition rate, density, and stress (3). Also we requested (Technical Status Report for December

1979) that Work Task 6 (preparation, evaluation, and delivery of solar cells) be eliminated with that effort switched to APFIM characterization (see Section II.D.).

II. EXPERIMENTAL

A. FILM PREPARATION

All films were prepared in an oil diffusion-pumped MRC Model 8500 single-target rf-sputtering module. The basic configuration of the sputtering system is shown schematically in Figure 1. The target was 13cm diameter polycrystalline Si (Specialty Metals, Inc.; 99.9999%) water-cooled through the packing plate, and sputtered at 100W forward power in all tests reported here. Pressure measurements were performed at ~ 1 mTorr with a capacitance monometer (MKS Baratron, Type 222) and at ~ 1 mTorr with an ionization gauge (NRC #831).

Ar (commercial grade), purified by flow through a Ti-getter over (R.D. Mathis #GP-100), and H₂ (commercial grade) flows were measured with mass flowmeters (Hastings-Raydist, Type H-5M and H-500, respectively). Ar flow was pressure controlled automatically (Graville-Philips Series 216 flow controller). Gas flow was through stainless steel tubing to adjacent leak valves (~ 1 cm apart) at the inside face of the chamber wall. No dopant gases were used. The substrate was thermally floating (i.e., normally considered by the misnomer "room temperature"). Target-substrate distance was 4.0cm, and all substrates were glass on resting upon glass placed on the A-substrate table. Substrates were cleaned by sequential ultrasonic baths in H₂O-detergent, H₂O, acetone, and ethanol. They were stored under ethanol and blown dry in N₂ immediately before placement in the vacuum chamber.

For each run, the system was prepumped for at least 4 hours to a base pressure of $< 5 \times 10^{-7}$ mTorr (which increased to $\sim 2 \times 10^{-6}$ upon throttling before sputtering gas admission). The chamber then was filled with H₂ to a given pressure and backfilled with Ar to a fixed total pressure. Both total pressure P_T , and H₂ partial pressure, P_H (taken nominally as pressure before Ar back-fill) were quite stable during the course of deposition, as observed by flow rates. Immediately before deposition, the target was presputtered for 15 minutes (under the same conditions as for deposition) onto a rotatable shutter.

Films were deposited with varied P_T and %H as shown below in Table 1:

Figure 1 Schematic of rf-diode sputtering system.

Table 1

P_T Torr %H	0.000	0.022	0.22	1.7	10.0
5	315	-	306	302	-
20	300	-	305	-	301
40	316	312	311	-	303
70	313	314	307	-	308

Sample numbers indicating combinations of P_T and %H used in this study.

%H is the fraction of H in the plasma [%H = $(P_H/P_T) \times 100\%$]. Ascending sample numbers follow the order of preparation. Before beginning this preparation series the chamber interior was cleaned to bare metal and, as indicated, the order of sample preparation was nonsystematic in an attempt to avoid biasing deposition conditions with run-to-run drift due to film build-up on walls, progressive development of minor air leaks, etc.

In discussing these films, we refer to samples by both sample number and the deposition conditions abbreviated as $P_T(\%H)$; e.g., sample #305 $\equiv$ 20mTorr (22%H), $\equiv$ 20mTorr (22%).

For each deposition, the following substrates were used: 1) a portion of a high resistivity c-Si wafer for IR-vibrational measurements, 2) optical grade fused silica (GE 125) for visible-near IR optical measurement, 3) de-oxidized stainless steel, and thick and thin glass cover slips of various sizes for various other measurements. The position of each substrate type was approximately the same for each run, and all were located under the target to within 3cm of the center, except for (8mm)² glass slips extending radially as far as 8cm to create steps for thickness measurements.

B. MICROSTRUCTURE

Chemical etching was performed on films deposited onto (2.5cm)² glass slides using reagent grade etchants. The etching-time dependence of texturing effects was investigated by successively immersing overlapping regions.

Microstructure and texture of 1) top surfaces and fracture edges for both etched and unetched material and 2) film areas subjected to $\sim 15\text{MeV } ^{19}\text{F}^{4+}$ bombardment during nuclear resonant reaction analysis for H, were observed with a JEOL JSM-50A SEM operated at 25KV.

Figure 2 shows representative SEM micrographs of etched and unetched films ($\%H = .22$, $P_T = 5, 2, 40, 70$) viewed so as to indicate surface morphology as well as internal microstructure at a fracture surface. The etchant used here was $HF:HNO_3:HAc = 1:1:1$. Figure 3 shows greater detail of etched and unetched top surfaces for $P_T = 5$ and 20mTorr. We see gradation of several film characteristics between low P_T and high P_T (for $\%H = .22$). At the lowest P_T , the films appear dense and uniform in the interior with no detectable surface roughness. Even upon extended etching, the surface of the low P_T films shows little relief. The small surface roughness that is observed at lowest P_T (Figure 3) upon etching might be due to poorly-defined anisotropic microstructure or perhaps simply to the artifact of dissolution kinetic effects during the etching of an isotropic material. In Figure 2(a), the columnar structure is seen near the top edge of the film fracture surface. It is noted that this may be indicative of residual microstructure; however, this effect was a rare occurrence in observations of the low P_T films. Indeed, these films generally showed no definitive microstructure, whether with or without etching. The structure in fracture surface as seen in Figure 2(a) could well be due to effects of stress—either internal stresses (discussed below) or non-uniform stresses at the crack front developed during fracture (commonly seen in the supporting glass which is also fractured in a similar manner at the same time).

At high P_T , distinct vertical columns are seen in the film interior and each terminates at the film surface with a "hemispherical cap". The columns on the order of $\sim 1000\text{\AA}$ in the etched fracture cross-sections (especially at $P_T = 70\text{mTorr}$) are due to silica gel (resulting from dissolution of glass substrate) redeposited at the surface and is not significant.

Figure 4 shows the surface fracture cross-section of a film prepared at 70mTorr (0%H). It is roughly similar in appearance to the films prepared at large P_T , but with .22%H.

Figure 5 shows the etch rate vs P_T for films prepared at 0 and .22%H. Concentrated HF was used as the etchant. A radical increase in etch rate for films prepared at higher P_T is observed. We note that the "etch rate" here includes not only chemical dissolution but also physical removal of film, as in film "flaking".

Figure 2 SEM micrographs of unetched (top and etched (bottom) fractured surfaces viewed at an angle so top surface can be seen. Glass substrate is at bottom in all cases. (a-d) are 5, 20, 40, and 70mTorr, respectively; all at 0.22%H.

Figure 2 (continued)

Figure 3 SEM micrographs of top surface of unetched (top) and etched (bottom) films at the lower gas pressures: a) 5mTorr (0.22%H) and b) 20mTorr (0.22%H).

Figure 4 SEM micrograph of film prepared
at 70mTorr without hydrogen.

Figure 5 Etch rate vs. total gas pressure at two different hydrogen percentages.

C. COMPOSITION

Electron Microprobe: $K\alpha$ X-ray intensities for Si and Ar were measured on a JEOL JSM-50A SEM with a KEVEX Energy Dispersive Spectrometer (Model μ X7100 multichannel analyzer). $OK\alpha$ intensities were determined on an ETEC Autoprobe using a gypsum crystal. In both cases $v = 15KV$ and $\phi = 36^\circ$. Standard intensities were taken from Si on c-Si, and for O on SiO_2 (quartz).

Cleaved single-crystal KCl was used as a hypothetical Ar standard. Since the intensity of emitted characteristic X-radiation in a given series is a continuous function of atomic number, $Z^{(42)}$ (and in fact is nearly linear in the region near $Z \approx 18^{(43)}$), we may use KCl as a hypothetical standard for Ar with the relationship

$$I_{Ar}^{100\%} = \frac{I_K^{100\%} + I_{Cl}^{100\%}}{2}$$

where $I_X^{100\%}$ are the hypothetical 100% weight standard intensities. The $I_{X=K,Cl}^{100\%}$ are obtained from the KCl intensities, corrected for mass and matrix effects (i.e. $I_{Ar}^{100\%} \approx I_{K(KCl)} + I_{Cl(KCl)}$).

The intensities were converted to weight fractions with the Colby MAGIC IV program⁽⁴⁴⁾. Only for oxygen were any samples below detection limit ($\sim 1\%$ by weight). Calculated total weights were systematically less than 100%: Samples with $>1\%$ weight O averaged 95% total weight; the average for all others was $\sim 92\%$ total weight with weight deficit roughly proportional to % O weight.

Independently determined H concentration (see below, IR and nuclear reaction analyses) were not included on the X-ray correction calculations; the presence of even $\sim 1\%$ weight H (maximum for our samples $\lesssim 1\%$ weight) will affect the intensity correction by less than 1% which is the approximate maximum precision of the technique itself.

Fresh fracture cross-sections of several films with a range of O content were examined in an attempt to detect any gross variations in vertical distribution of O (primarily post-deposition; see below) which might result in systematic deficits in calculated weight. In all cases, O was found to be uniformly distributed with a "bulk" concentration in good agreement with "surface" concentration. Figure 6 shows Ar profiles for several films prepared under different conditions.

Figure 6 Argon depth profiles.

After adding H concentrations (see below) to the values for Si, O, and Ar, all values were normalized to 100% weight and expressed in terms of atomic fraction. Figure 7 shows the P_T dependence of these values. Figure 8 shows the correlation of Ar and O content for the films prepared - a marked inverse proportion is observed.

IR Vibration Spectrometry: IR transmission spectra were recorded for all films in the region 400cm^{-1} to 3000cm^{-1} with a dual beam IR spectrometer (Perkin-Elmer 580). Spectra, recorded within a few weeks of preparation, are shown in Figure 9. Transmission values in the region 1900cm^{-1} to 2300cm^{-1} were digitized and converted to absorption coefficients in the manner described by Brodsky⁽⁴⁵⁾ (Figure 10). The stretching modes for monohydride (w_1^S), dihydride (w_2^S) and trihydride (w_3^S) at 2000cm^{-1} , 2090cm^{-1} , and 2140cm^{-1} , respectively⁽²⁴⁾, were unfolded with a computer program assuming a Gaussian distribution.

This procedure involves the assumption of $\sigma \approx 40\text{cm}^{-1}$ (consistent with observed isolated peaks). Peak maxima are calculated by subtracting the contribution at that position from neighboring peaks. Individual peaks are then constructed (the area of the absolute value of the residue was always less than 10% of the original area, and is apparently due to non-Gaussian "tails"). The residue at each point is then subtracted from the constructed peaks in proportion to their magnitude, so that the total area of the original peak cluster is conserved.

The concentration of Si-H bonds of each type and total H concentration were calculated, again as described by Brodsky⁽⁴⁵⁾, but with the reestimated local field correction established by correlation of IR-determined H concentration with nuclear resonant reaction determined H⁽⁴⁶⁾. The results are shown in Figure 11. This correction factor has since been shown to be in good agreement for H determined by nuclear reaction, thermal evolution of H_2 , and IR calculations.⁽⁴⁷⁾

Jeffrey⁽⁴⁸⁾ has performed similar measurements of rf-sputter-deposited a-Si:H prepared at larger rf-powers and shorter target-substrate distances. Our results conform to his in this respect: films with predominant monohydride content and no detectable dihydride and trihydride as indicated by the absence of bending mode absorption at $\sim 890\text{cm}^{-1}$ (w_2^B) and $\sim 845\text{cm}^{-1}$ (w_3^B) have an apparent strong asymmetry of the w_1^S mode (at $\sim 2000\text{cm}^{-1}$), vis, a broad tail on the high energy side extending through the w_2^S and w_3^S regions (see discussion). This effect

Figure 7 Normalized compositional data for the complete series of films.

Figure 8 Ar-O relationships at different hydrogen gas percentages.

Figure 9 IR spectral measurements for the complete series of films.

Figure 10 IR absorption coefficient data for the different gas mixtures.

Figure 11 Si-H bonding as a function of the sputter gas composition.

is observed in samples 302, 305 and 306. (Figures 9 and 10). The results of the original calculation for these have been corrected by estimates of dihydride and trihydride content based upon w_2^B and w_3^B absorption⁽⁴⁵⁾. Total hydrogen as estimated from the sums of the individual H configurations are shown in Figure 12.

In addition to these measurements, which were made shortly after fabrication (samples being stored in a vacuum desiccator for up to two weeks prior to analysis), measurements were made after film storage at ambient conditions for ~6 months. For these spectra, qualitative observations only were made.

Nuclear Reaction Analysis: Hydrogen depth profiles were obtained using the $^1\text{H} (^{19}\text{F}, \alpha\gamma) ^{16}\text{O}$ resonant nuclear reaction technique at the Oak Ridge National Laboratory Tandem Van de Graff accelerator facility. This technique and an analogous one based on $^1\text{H} (^{15}\text{N}, \alpha\gamma) ^{12}\text{C}$ are described in greater detail elsewhere⁽⁴⁹⁾.

The technique relies on the narrow isolated nuclear resonance occurring in the solid sample as an accelerated beam impinges at normal incidence to the sample surface. When beam energy equals the resonance energy, the reaction occurs at the surface and to a depth dependent upon the resonance energy width and the stopping power of the target. The number of δ -rays with the corresponding resonance energies emitted is proportional to the average H concentration in that depth interval. At higher energies the reaction occurs at a depth below the surface determined by the stopping power of the sample. However, the depth interval over which the resonance energy will exist is now increased (i.e., depth resolution is decreased) by an energy straggling factor. For example, with the 16.44 MeV resonant reaction $^1\text{H} (^{19}\text{F}, \alpha\gamma) ^{16}\text{O}$, depth resolution is ~250 Å at the surface and ~300 Å at a depth of 4000 Å in Si. In principle, quantitative H depth profiles can be calculated with knowledge of 1) the density and stopping power of the sample, 2) the γ -ray yield as a function of beam energy, and 3) the contribution to γ -ray yield due to other resonances and off-resonance interactions with hydrogen at depths outside the interval being probed at a given energy.

Although the reaction $^1\text{H} (^{15}\text{N}, \alpha\gamma) ^{12}\text{C}$ is also suitable for this type of measurement and has some advantages over the ^{19}F -beam technique [superior depth resolution, greater accessible depth range (several μm 's in Si), and simpler data corrections for off-resonance interferences], a ^{19}F beam was used because of difficulties (not atypical) in obtaining a stable negative ion ^{15}N beam

Figure 12 IR determination of hydrogen content for the various films.

source.

We used a $^{19}\text{F}^{4+}$ beam and the 16.44 MeV resonance producing 6.1, 6.9, and 7.1 MeV γ -rays. A second resonance at 17.56 MeV limits the useful depth range to $\sim 4000\text{\AA}$ in silicon although this range can be extended with appropriate deconvolution of data.

The different H^+ -implanted c-Si reference standards were analyzed along with the unknown samples. Calculated standard intensities [γ -ray yield (10^{22}H atoms/cc) / $\ln A^{19}\text{F}^{44}$] were in agreement. Hydrogen concentrations in terms of #H atoms/cc were estimated from normalized γ -ray measurements and standard intensities with the assumption that the density and stopping power of the sample were the same as those for c-Si. The nine samples analyzed were all $> 5\mu\text{m}$ thickness, and thus were treated as if infinitely thick, allowing the contribution of low energy resonance and off-resonance contributions to the observed γ -ray yield to be accounted for by a single measurement slightly below the resonant energy (16.41 MeV).

Atom Probe Field Ion Microscopy: We have recently developed a new atomic-scale thin film characterization in which the film is deposited directly onto a field ion microscope tip⁽³⁰⁻³¹⁾. In the present case, we deposited both undoped and P-doped a-Si:H films onto W tips and then imaged and mass analyzed them in a high-performance atom probe field ion microscope (in the Field Emission Laboratory under the direction of T. T. Tsong). The above references contain details of this instrument and new technique.

The films studied were all deposited at the same conditions: 20mTorr (0.22%H). The FIM images were similar to those reported for a-Ge and a-Ge:H⁽³¹⁾. However, the main object of this preliminary study was to mass analyze the hydrogenated a-Si films. Accordingly, these experiments were done "blind" in vacuum since no hydrogen could be introduced as an imaging gas⁽³⁰⁾ due to interference. The thin films ($\sim 1000\text{\AA}$) were pulse evaporated and vapor species recorded. The table below are the species collected after removal of the top layers containing adsorbed gases and before the substrate was reached.

Considering only the Si-containing species, the apparent composition of this film is $\text{SiH}_{0.45}$. Since field dissociation (of vapor species) is a possibility but field association is highly unlikely, the SiH_3 species must represent real units in these films. Although trihydride units have been suggested on the basis of IR spectral measurements⁽²⁴⁾, this is the first direct confirmation of their existence. Since dissociation would always give the lower

hydrogen-containing units, the real composition of the bonded Si-H would be greater than SiH_{0.45}. Some of the H⁺ species could be field dissociation products but certainly not all; which leads to the question of the origin of the remaining H⁺. Possibilities include the existence of free hydrogen or adsorbed water vapor. This and other questions, such as the atomic scale distribution of hydrogen and dopant atoms, will be addressed in future studies.

Table 2

<u>Species</u>	<u>No.</u>
H ⁺	82
OH ⁺	4
SiH ²⁺	1
(SiH ₂) ²⁺	4
Si ⁺	31
SiH ⁺	11
SiH ₂ ⁺	1
SiH ₃ ⁺	2

Ion Species Obtained on Field Evaporation
of a-Si:H Sputtered Films on W tips.

D. VISIBLE/NEAR IR OPTICAL ABSORPTION:

Striking differences in film transmittance were evident by sample visual examination. In viewing the light transmitted in samples of similar thickness, we see a trend of increasing intensity and color shift consistent with the shift of an optical bandgap from the infrared to the visible. For example, with the series of films prepared at 20mTorr total pressures, film appearance by transmitted light progresses from opaque at 0%H to red-orange for 10%H. Even for films prepared with no H in the plasma, the shift of the absorption edge with increasing total pressure was evident in this manner.

Optical bandgap absorption is given by the following equation (50):

$$h = \beta(\alpha h\nu)^{1/2} + E_o$$

where: $h\nu$ = photon energy; β = constant; α = absorption coefficient; and E_o = optical bandgap.

Although only thicker films ($\sim 10\mu\text{m}$) were prepared to date (necessary for our initial etching and microstructural studies), and thus restricting our absorption measurements to low photon energies, we nevertheless carried out these measurements in this limited range in order to at least estimate a bandgap and study the relative variations with preparation conditions.

We examined the vis/near IR optical absorption of the films in the absorptivity range $\alpha \approx 10^3 \text{ cm}^{-1}$ to 10^4 cm^{-1} . Film thickness, t , ranged from 5.0 to 12.0 μm . In this situation, the transmittance, T , can be approximated⁽⁵¹⁾:

$$T \approx \frac{(1-R_1)^2 e^{-\alpha t}}{1-R_1^2 e^{-2\alpha t}}$$

where R_1 is the reflectance of the film-air interface. A further approximation of $R_1 = R_2$ (where R_2 is the measured reflectivity of the air-film-substrate system) is found to introduce negligible error for the ranges of α being investigated.

The high energy portion of the optical absorption curve $\alpha(h\nu)$ in general⁽⁵²⁾ and for a-Si:H in particular⁽⁵³⁾ is described by:

$$\alpha(h\nu) = \beta(h\nu - E_0)^2/h\nu$$

where E_0 is the optical gap between valence and conduction bands with a density of states with the form $N(E) \sim E^{1/2}$. E_0 is the intercept of the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curve.

Although our measurements were restricted to relatively small α 's, the measurements do extend far enough to extrapolate E_0 , as is indicated by the linearity of our $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curve and the results of other studies⁽⁵⁾ of similar rf-sputter-deposited a-Si:H films.

A Cary 14 spectrometer was used for all transmission measurements and a Beckman DK-2A spectrometer with a specular reflectance attachment was used for all reflectivity measurements.

Figures 13 and 14 show the absorptivity vs. photon energy for the samples in terms of P_T (Figure 13) and %H (Figure 14). The shift of absorption to higher energies, both with increasing P_T and increasing %H, is evident and is also seen in Figure 15, in which the optical bandgap (determined as described above) is plotted as a function of %H in the plasma for the various P_T 's.

E. SUBSTRATE SELF BIAS-VOLTAGE

The substrate self-bias voltage, V_{sb} , was measured as a function of P_T (%H) and input power in a separate experiment. An electrically isolated conducting film with electrical contacts isolated from the plasma by a ceramic mask was used as the substrate and voltage sensor. The potential, relative to ground, of the substrate/deposited film was monitored as during normal film preparation. The results are shown in Figure 16. Figure 17 shows the relation-

ship between P_T and V_{sb} at 100W power, as well as the atomic ratio, Ar/Si, for prepared films. (It is noted that T. D. Moustakas obtained essentially an identical V_{sb} vs. P_T curve (Figure 16) in his sputtering experiments, as reported in his review talk after ours at the a-Si/Materials Contractors Meeting at Dulles International Airport, April 1980).

Figure 13 Optical absorption coefficient data showing bandgap shifts with %H at the various P_T's.

Figure 14 Optical absorption coefficient data showing effect of P_T on bandgap at various %H's.

Figure 15 Optical bandgap (E_0) vs. %H.

Figure 16 Substrate self-bias floating potential as a function of P_T for various rf-power levels.

Figure 17 V_{sb} and Ar/Si ratio versus P_T .

III. DISCUSSION

A. INTRODUCTION

We find that the film characterization and their variations, as described above, are generally consistent with fundamental plasma and film growth processes which can be understood for reactive rf-diode sputtering in this range of P_T and %H. We can describe the sputtering of Si with Ar in H_2 in this system, i.e., physical sputtering in a reactive ambient, by separating these processes into two categories: (1) physical film growth as described by the structure zone model (SZM) and (2) plasma Si-Ar-H chemistry. The general features of each of these general processes are first briefly described. In the following section the details of the dependence of observed film properties upon P_T and %H are discussed in terms of these basic controlling processes.

The Structure Zone Model: The Structure Zone Model (SZM) originally proposed by Movchan and Demchishin and generalized and expanded by Thornton⁽⁴¹⁾, explains the mechanisms by which the deposition parameters total pressure, P_T , and T/T_m (T_m = film material m.p. and T = film temperature during preparation) control film microstructure. The SZM is applicable to all types of physical vapor deposited (PVD) films because the atomic processes upon which it is predicted are quite general. The vapor-solid transformation is idealized as occurring in three basic steps: (1) vapor atoms impinge on the film, transferring kinetic energy and becoming loosely bonding adatoms, (2) adatoms undergo surface diffusion until they are trapped at a low energy site (or are desorbed), and (3) the incorporated atoms readjust their positions by bulk diffusion. P_T influences the angular distribution and energy of the incoming vapor flux (step 1) and T/T_m controls surface and bulk atomic mobility (steps 2 and 3).

Figure 18 is a schematic representation of the structure zone model, as developed by Thornton for metal sputter-deposited films, showing the four zones. In zone 1, surface and bulk mobility are negligible. At high deposition pressures (or with the vapor source at oblique incidence) "shadowing" effects due to preferential vapor deposition at film (and/or substrate or nucleus) surface projections will occur. In this way, nuclei will grow in isolated columnar islands with some volume of void or low density regions separating the islands.

We note a striking demonstration of this dependence of film microstructure on angular distribution of the incident flux for rf-sputtered SiO_2 as reported (without explanation) by Hara⁽⁵²⁾. Two films were deposited from an SiO_2

Figure 18 Schematic of Structure Zone Model (Reprinted with permission of J. A. Thornton).

target in a magnetron rf-sputtering system at 5×10^{-3} Torr Ar with the incident flux at $\sim 45^\circ$ from normal in one case and at normal incidence in the other. Films deposited at 45° incidence exhibited anomalous etching (HF) behavior, etching occurring preferentially in vertical channels with about 100X greater etch rate than for the columns themselves (i.e., revealing a Zone 1 structure). Films deposited at normal incidence exhibited uniform etching. Similarly, our detailed etching studies on a-Ge films deposited on "rough" metal substrates demonstrates clearly the effect of macroscopic surface projections on Zone 1 growth⁽³³⁾.

In zone T, P_T is low enough and T/T_m high enough to allow coalescence of growing nuclei, producing a film with density approaching bulk values. However, an array of poorly defined, very fine fibrous columns have been revealed by etching of a-Ge^(32,33) and a-Si⁽³⁴⁾ sputtered films for what would be considered zone T structure films. This structure is evident in cross-section and at the surface as very fine hemispherical surface projections. This fine structure is often difficult to resolve but is present as a substructure in the columns of zone 1.

Zones 2 and 3, as we have recently pointed out⁽³³⁾, apply only to crystalline films. Zone 2 consists of a dense columnar grain structure in the range $T/T_m \sim 0.3$ to 0.5 . Here adatom surface mobility is sufficiently large to permit existing crystallites to grow by localized epitaxy, producing columnar grains. Zone 3 occurs at even higher T/T_m , consists of equiaxed grains throughout the film bulk, and is a result of recrystallization and domination of bulk-diffusion processes.

We can now consider additional "physical" phenomena which may be important in rf-diode sputtering as compared to vacuum evaporation at low pressures:

(1) the presence of sputtering gas, (2) sputtered atoms leaving the target at much greater than thermal velocities, and (3) energetic bombardment of the growing film by (a) negative and neutral ions from the region of the target, (b) positive ion bombardment due to substrate self-bias, and (c) plasma electrons and x-radiation.

Sputtering gas (and other plasma species if present) will be adsorbed on the surface of the growing film, thus decreasing the surface mobility of the principal atoms and possibly, becoming incorporated in the growing film, either in "void" or low-density regions of zone 1 or in the "bulk".

Atoms sputtered from the target possess significant energies on the order of 10-100eV, and may reach the substrate without atomic collision in the low pressure regime, where the mean free path, λ , approaches the target-substrate

distance, d_{TS} .

Energetic bombardment of the growing film is probably the most important deviation from the SZM picture. For example, depending on M_I/M_T , where M_I = mass incident atom, M_T = mass target atom, inert gas ions can be reflected as neutrals with large fractions of the energy gained in the acceleration of the positive ion through the dark space, energies on the order of 1 KeV. At this energy level, resputtering or implantation become important. In the same manner, negative species formed at the target surface will be accelerated directly toward the substrate with similar energies. A third source of energetic atomic bombardment results from positive ions being accelerated toward the film itself if it is electrically biased. Aside from intentional biasing (bias sputtering technique), a bias as large as hundreds of volts (negative) relative to the plasma can be induced in electrically insulating (or insulated, i.e., floating) films, especially at low pressures and arising in the same manner as does the target self-bias voltage. For example, Jones et. al.⁽⁵²⁾ has shown that floating potentials of -130V exist in (electrically floating) sputtered Si films rf-sputter-deposited at low pressures (2mTorr); the re-emission coefficient due to Ar^+ bombardment in this case is 0.2 (i.e., the deposition rate is decreased by resputtering to about 80% of the "expected" rate).

Electron and x-ray bombardment are generally occurring phenomena in the rf-sputtering process in which electron bombardment is enhanced at low pressures where the electron mobility is greatest.

Plasma Chemistry: Aside from the work performed by Matsuda, Nakagawa, Tanaka, et al.⁽⁵³⁾ (referred to as MNT), no direct measurements have been made of the a-Si:H reactive rf-diode sputtering plasma environment. Indeed, there is very little speculation even as to plasma chemistry and related effects in the interpretation of deposition parameter control over final film properties. Fortunately, MNT have investigated the plasma photon emission in the same region of deposition space in which we have worked. Extending their findings with some basic concepts in plasma chemistry and ion-solid interaction energetics, as well as some of our measurements, we will suggest a broad picture of the essential role played by plasma chemistry in the formation of rf-diode sputtered a-Si:H films.

MNT describe the variation in the relative amounts of H_2 , H, SiH_4 (all $Si_x H_y$) and Ar (without respect to electron configuration or charge) as indicated by plasma photon emission. They find significant amounts of H and SiH_4 (relative to H_2 and Ar) in almost all cases. They have investigated three situations in detail:

- 1) For 20% H at $P_T = 10$ mTorr and 150W input power, they observe, in the vertical distribution from target to substrate, roughly constant-proportion amounts of H, H_2 , Ar, and SiH_4 in the plasma glow, with a very pronounced abundance of H near the plasma edge of the target dark-space.
- 2) For 10 mTorr total pressure and 150W, as the plasma composition is varied from 100% to 0% H_2 (i.e., from 0% Ar to 100% Ar), they observe for the non-spatially-resolved emission (a) the expected linear increase in Ar, (b) a very sharp increase in H and a super-linear decrease in H_2 (H peaking around 80% Ar), and (c) a plateau in SiH_4 emission which extends from ~80% to 20% Ar.
- 3) For 150W power, as the deposition pressure increases, Ar, H_2 , and SiH_4 intensities increase slowly, but H intensity increases greatly.

We will discuss below their interpretation of their corresponding film IR vibrational spectra along with our own, but first we make several points on interpretation of plasma interactions.

First, MNT do mention that the reaction $H_2 \rightarrow H$ is promoted by incorporation of Ar into the gas, but they give no explanation of this interaction and state that "Hydrogen gas introduced into the sputtering chamber is excited and decomposed into H atoms (or radicals) where the electric field is strongest". We suggest that the primary mechanism is $Ar^+ + H_2 \rightarrow ArH^+ + H$. This reaction has been used by Lampe⁽⁵⁴⁾ to produce atomic hydrogen. As described by Libby⁽⁵⁵⁾ Ar^+ is isoelectronic with Cl, and thus the simple electron affinity arguments that explain the stability of HCl can be used to explain the stability of ArH^+ . Indeed, unless this molecule is neutralized, it should actually have a stronger chemical bond than HCl because the extra positive charge on the Ar^+ nucleus causes the electron energy levels to lie below those of Cl.

Second, it is well known that H^+ contributes strongly to the positive ion

current at the cathode. This is generally apparent as a decrease in the deposition rate with increasing H_2 in the plasma. This is not only because H^+ will contribute to the cathode current with negligible sputtering yield but also because the high ionic mobility of H^+ relative to Ar^+ will allow H^+ to constitute a disproportionately large share of this ion current as compared to Ar at the cathode⁽⁵⁶⁾. This reasoning could also explain the large H-intensity peak near the cathode in the MNT data.

B. GENERAL

We first note that the SEM micrographs of Figures 2, 3 and 4 are the first direct demonstration of the anisotropic microstructure of rf-sputter deposited a-Si:H films, although the presence of microvoids has been inferred by several groups. For glow discharge (GD) a-Si:H films Knights and co-workers have made detailed studies of film microstructure and many properties dependent thereon⁽¹⁹⁻²⁹⁾.

The microstructures of the films examined here are consistent with the Structure Zone Model as well as with several of the film properties which we have evaluated. We have previously shown that a-Ge⁽³³⁾ and a-Si⁽³⁴⁾ sputtered films can be understood and classified on the basis of the SZM, and this study shows that its range of applicability extends to hydrogenated a-Si films. First, it is expected from the SZM that as P_T is increased, film microstructure moves away from zone T and toward zone 1, as seen in Figure 2 ($P_T = 5, 20, 40, 70$ Torr, %H = .22). The film microstructure, as seen directly in the unetched specimens and as "revealed" in the etched ($HF:HNO_3:HAc = 1:1:1$) specimens, makes a transition from an apparently totally isotropic material to an increasingly "open" and columnar, anisotropic morphology. Second, this transition is also observed indirectly in the degree of post-deposition oxidation and the etching behavior (Figures 7 and 5, respectively). Thus we can assume that the degree of post-deposition oxidation is roughly proportional to the "porosity" and that the etching rate with HF corresponds to the amount of oxide formed.

For the films prepared at the higher gas pressures (40 and 70 Torr), we note several major effects due to H. For instance, the surface and fracture cross-sections of 70 Torr (0%) (Figure 4) and 70 Torr (.22%) [Figure 3(g)] are generally similar in their microstructure, yet the film prepared with 0% H is about 35% denser than that prepared with .22% H (Figure 2 in 3rd Quarterly

Report). These two observations are consistent with the assumption that small amounts of H (here 0.22%) do not significantly affect the physical sputtering processes but do effect chemical processes. Since H in the plasma is not expected to change the angular distribution of sputter-deposited species, the SZM (which is based on physical processes) can explain the similar microstructures. In order then to explain the differences in density, it must be considered that the volume of low density, intercolumnar regions is about the same both with and without H. Although it might simply be argued that H-substitution for Si could account for these density deficits, the exact distribution of H in this nonuniform material is still unresolved. It has been suggested previously for glow discharge a-Si:H that these polymeric-like materials consist of Si:H/SiH_x, column/intercolumn regions; our microstructural, density, and IR spectra results are similar to theirs. However, there has been no direct measurement of this H-segregation at the low-density intercolumnar regions.

The decrease in compressive stress both with increasing %H and P_T (see Figure 3 or 3rd Quarterly Report) may be understood with regard to either H within the columns (Si:H) or low density SiH_x polymers in the intercolumnar and/or columnar regions. As suggested by Revesz⁽⁵⁷⁾, the essential role of H in a-Si:H is that the a-Si structure is relieved from its obligation of all Si atoms being bonded to other Si atoms in the rigid tetrahedral configuration. Thus, especially for SiH₂ bonding, an appreciable flexibility is imparted to the a-Si:H structure relative to a-Si. Although the mechanisms for intrinsic stress generation in thin films is not well understood and a variety of mechanisms have been proposed⁽⁵⁸⁾, we can expect that this increased structural flexibility will possibly decrease stress generation (for example, by the increased freedom of bonding as columns coalesce during growth) and/or by simple elastic accommodation of stresses being generated by some independent mechanism as the film grows. Based on the observation that as the columnar microstructure becomes more pronounced the intercolumnar regions increase in width, the following mechanism is one possibility: stress is generated at the column-intercolumn-column boundaries and that stress relief, as suggested by Revesz⁽⁵⁷⁾, would be directly proportional to the intercolumnar width.

In films prepared at the lowest total gas pressures, we see radical differences in film properties: monohydride favored over dihydride, high intrinsic compressive stress, very low susceptibility to post-deposition oxidation, and high Ar content.

The Ar content is as high as 7.1% for 5 μ (0%), but only $\sim$ 0.5 at% for 70 μ (0%) [Figure 7(c)]. Considering that the Ar concentration in the plasma at the higher P_T must be $\sim$ 35 times larger than that at the lower P_T , simple "entrainment" of adsorbed Ar by the growing film must be discarded as an important process here. Also, single-collision, elastic backscattering of target-surface-neutralized Ar^+ which has been accelerated in the target dark-space can be discounted; such single-step backscattering is not possible because of the larger mass of Ar as compared in Si and the fact that momentum must be conserved in such a process.

Looking now to the substrate self-bias voltage, V_{SB} , as measured with respect to ground (Figure 16), we find that its value drops sharply at low pressures. At $P_T = 5\text{mTorr}$ (Power = 100W) $V_{SB} \approx -10\text{V}$. Although the plasma potential was not measured, it is expected to be larger than +20V (again with respect to ground) since plasma potentials are always higher at lower gas pressures. This high negative potential of the growing film surface relative to the plasma potential will accelerate Ar^+ ions from the plasma toward the film. While this potential may be insufficient for implantation, it is near or above the sputtering threshold voltage. Thus, preferential resputtering or just increased surface adsorption of Ar, to the point that will account for the observed levels of Ar in the film, must be considered. Also, the possibility of noble gas entrapment through metastable atoms has been suggested⁽⁵⁹⁾. Substrate self-bias voltage and atomic % Ar are plotted in Figure 17. It is difficult to speculate as to atomic position of Ar in the film. However, it is suggested by the IR thermal decomposition studies of Tanaka, et al.⁽⁶⁰⁾ that films with high Ar content (both SD and BD-catholde) behave fundamentally differently than films with low Ar content, and that Ar seems to inhabit a structural void associated with dihydride. To the contrary, for our films high Ar contents are associated with high monohydride contents. We have no reason to expect this to be a causative relationship. Although Ar incorporation may be associated with processes at coalescing column boundaries, for our materials Ar content is greatest for the films which display the least microstructure. The positive correlation between Ar content and the intrinsic stress suggests possible uniform entrapment of Ar into the relatively open Si tetrahedral structure. The marked decrease in post-deposition oxidation with increasing Ar content (Figure 8) also suggests that the absence or drastic reduction of inter-columnar channels for migration of oxygen into the film in these high-Ar films.

One of the more significant features of the films prepared at low P_T is the predominance of H bonded as monohydride. This is generally a strong indication of films suitable for photovoltaic applications⁽⁶¹⁾. Jeffrey et al.⁽⁴⁸⁾ have demonstrated a similar control of dihydride/monohydride bonding in a similar sputtering system, but at higher P_T (~30-150mTorr) and higher power (up to 600W). They conclude that the plasma ion temperature controls the H bonding configuration because energetic particles incident upon the growing film surface break dihydride bonds preferentially over monohydride bonds. Anderson⁽⁴⁾ and Pawlewicz⁽¹⁴⁾ also cite energetic ion bombardment as an important process in controlling film properties at low P_T , but indicate only detrimental effects of this bombardment. One tentative explanation of our data is that the high negative film potentials (relative to plasma potential) at low pressures lead to Ar ion bombardment which, in turn, leads to dissociation of SiH₂ bonds at the film surface preferentially and to a minimization of the inter-columnar regions.

We also consider the bombardment effects due to H. As discussed previously, $H_2 \rightarrow H^+$ is observed as a major reaction in the plasma, and indeed H^+ current to the target dominates over Ar^+ current because of the greater mobility of H^+ (also indicated by the decrease in deposition rates with increasing %H and by the H emission peak near the outer side of the cathode dark space in the work of MNT). Although not discussed previously, we suggest the possibility that H^+ is accelerated across the target dark space, is neutralized and back-scattered at high energy [with up to 90% of the cathode potential (here ~1000V) for a single elastic collision with reflection at 180°], and that at a higher enough %H and large enough mean free path, λ (i.e., low enough P_T), H is incident upon the growing film with energies on the order of 1000 eV. Thus H-bombardment could also account for the monohydride content of the film by (a) dissociation of dihydride both at and below the surface due to energetic bombardment, or (b) direct formation of monohydride by implanted H⁽⁶²⁾ since

$$\left(\frac{\partial x}{\partial E} \sim 10 \text{ \AA/keV for H in Si} \right)$$

We note that for $P_T = 5\text{mTorr}$, the dihydride fraction increases from 0% of all H at .22% H to about 40% of all H at 10% H. This then indicates that monohydride formation (dihydride rearrangement) by the above two possible mechanisms might be balanced by dihydride formation controlled by the degree of surface coverage by H (as for the high P_T films with high dihydride).

We note here the asymmetry of the monohydride peak which is observed when dihydride content is low. The high energy shoulder observed for $P_T = 5$ and 20, of Figure 10(b) (and also observed by Jeffrey⁽⁴⁸⁾), which has been suggested to be due to the distribution of monohydride among several sites⁽⁶²⁾, is not readily apparent in any other GD or SD a-Si:H described to date. It is clearly evident in the IR spectra of H implanted c-Si⁽⁶²⁾, but disappears after annealing or Si implantation.

In this connection we mention that while T_s was not controlled or even measured, substrate heating effects could become important, especially at low P_T where electron, neutral, and ion bombardment increase dramatically. Floating substrate temperatures under these conditions can easily reach $\sim 200^\circ\text{C}$ by our experience. Measurements of the growing film temperature, though obviously important, have not been made by anyone as yet. Such measurements, as described by us previously⁽⁶³⁾, are in progress.

We mention that the optical bandgap, estimated as described above, is at the near optimal value of 1.5 eV⁽⁶⁴⁾ for the films with high monohydride content [5mTorr (.22%, 1.7%)]. Whether or not these films are well suited as photovoltaic materials in other respects is to be investigated with Schottky Barrier test devices. Also, it is noted that the saturation of the bandgap at ~ 2.0 eV for high P_T and high % H is as previously observed. Although our optical measurements are not highly refined, we would like to note that variations in density, post-deposition oxygen content, and possibly Ar content, can have strong effects on correlations of the measured gap with H bonding effects, etc., and that interpretation of optical data should be performed within the framework of a total physical and chemical characterization. For example, films prepared without intentional addition of H show an increase in the gap of over 0.5 eV as P_T is increased from 5mTorr to 70mTorr [Figure 14(a)]. Referring to Figure 7(d), we see, however, that O content has increased from not detectable to almost 10 atomic % over this range, and is probably responsible in total for the observed "shift" in the gap. Similar trends are seen at other % H.

IV. CONCLUSIONS

Below are listed summaries of the significant accomplishments. The details of each accomplishment are included in the Quarterly Reports and this Final Report as are the details of the preparation of our systematic set of samples.

- * The a-Si:H films could be anisotropically etched in a manner similar to that previously found for a-Ge^(32,33) and a-Si⁽³⁴⁾. The resulting film microstructure is a dense array of columns with a spacing on the order of 1000-3000 Å. The total surface reflectance is decreased from ~40% (for a smooth, as-deposited film) to ~3% for the etched film.
- * It has been shown that both a-Si and a-Si:H films can be classified according to the Structure Zone Model⁽³⁴⁾ and thus provides a means of comparing various samples made in a single study or samples from various laboratories. Since it is well established that the microstructure of a-Si:H films has an important effect on resulting film properties⁽²²⁾, this classification scheme should be important. Further, the anisotropic etching behavior is useful in that it more clearly reveals the microstructure such as in films which would otherwise display conchoidal fracturing. Also, the etching behavior is expected to be related to post-deposition oxidation and the porous nature of this material.
- * We have shown, for the first time apparently, that rf-sputtered a-Si:H films have a columnar microstructure similar to that reported for glow-discharge samples⁽²²⁾. The columns are aligned in the direction of the impinging vapor stream. In addition to our etching studies for revealing this microstructure on the 1000 Å level, some preliminary APFIM and TEM experiments on a a-Si:H and a p⁺-doped a-Si:H films occurs at the ~100 Å level as well, indicating that the microstructures of a-Si and a-Si:H sputtered films are qualitatively similar. We have previously shown this same result for a-Ge and a-Ge:H sputtered films⁽³¹⁾.

- * We have prepared sputtered a-Si:H films which contain a predominance of monohydride units ($2000\text{cm}^{-1}/2090\text{cm}^{-1}$ IR peak ratio of $\sim 3-5$) and have no noticeable post-deposition oxidation as detected by IR measurements. The IR spectra for our samples prepared at 5mTorr total pressure (Ar + 0.22% H_2 and Ar + 1.7% H_2) are very similar to that reported by Knights et al.⁽²¹⁾ for their low power anode samples prepared by glow discharge, which were reported to have the lowest defect density, highest resistance to post-deposition degradation, and good physical property characteristics for device applications. In all previous reports on IR spectra of sputtered a-Si:H the highest 2000/2090 ratio has been ~ 1 ⁽⁵⁾. Since this may represent a significant advance in the sputtering preparation technique, further evaluation on these samples is to be continued.
- * We have measured, for the first time, the H, Ar and O contents of a systematic series of a-Si:H films. The H content ranged from 2 to 25 at % with the apparent best films (at 5mTorr) containing 17 at %H. Preliminary trends show that Ar-content increases with decreasing sputtering gas pressure while O-content increases with increasing pressure. The O-content data directly correlates with IR measurements and indicates that post-deposition oxidation is greater at the higher gas pressures. This behavior appears to be directly related to the void, or low density, structures present in these materials. Further correlation studies are in progress.
- * The high monohydride content, high Ar content, low post-deposition oxidation, and absence of microstructure at low gas pressures are all relateable to a probable Ar ion bombardment effect of the growing film which increases with decreasing sputtering gas pressure. However, high energy ($\sim 1000\text{eV}$) H-bombardment effects are also a possible explanation. Nevertheless, it is apparent that bombardment effects are responsible for the beneficial effects described above.

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