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

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INTRODUCTION

Hydrogenated a-Si solar cells have been prepared by both rf-sputtering and plasma decomposition. To date, only smooth, planar surface devices have been studied. We have found that for a-Si^(1,2), and for the analogous material a-Ge^(3,4), the surface microstructure of sputtered films can be altered by a simple post-deposition etching process and controlled by varying the film preparation conditions. We have demonstrated, in our proposal, that such textured surfaces can be advantageous in increasing the efficiency of Schottky-barrier type MS and MIS solar cell structures by decreasing visible reflectance from ~45% to less than 2%. Our overall objective in this contract is to develop the basic and applied understanding of film preparation and characterization, etching behavior, and solar cell device fabrication and measurements, such interrelated studies being necessary for assessing the potential of these textured surfaces. Of course, unetched, planar surface films will also be studied to form a basis for comparison. A number of questions still remain such as the effect of hydrogen on etched surface texture, whether or not preparation conditions for efficient cells correspond with conditions for useful texture, the ability to coat textured surfaces in order to form Schottky-barriers, etc., and, in large part, they define the direction of our research.

This anisotropic etching phenomenon is due to a rapid etch rate (oxidation, dissolution, and removal of reaction product) down void, or low density, regions followed by a slower etch rate perpendicular to the void surfaces. For black a-Ge^(3,4) and a-Si⁽²⁾ rf-sputtered films the resulting film microstructure is a dense array of aligned acicular columns. Such columns are aligned over rather large distances (>20 μ m) with the columnar alignment in the average direction of the condensing vapor species. We have shown for a-Ge that this etching clearly reveals the microstructure of these amorphous

films and allows us to classify the various films⁽⁴⁾ in terms of the Structural Zone Model^(5,6). In addition to these etching studies, we have recently shown directly, by field ion microscopy^(7,8) that the voids, or low density regions, and therefore the columns, in both a-Ge and a-Ge:H films⁽⁸⁾ originate at the film-substrate interface and are highly aligned. Thus, the complete picture at least for a-Ge, seems to be that there are three distinctly different columns present - macrocolumns ($\sim 2 - 10\mu\text{m}$ dia.), columns ($1000 - 3000\text{\AA}$ dia.) and microcolumns ($50 - 200\text{\AA}$ dia.) with corresponding macrovoids, voids, and microvoids.

Since a-Si films display similar microstructures, the structure zone model should prove useful as a scheme for classifying and understanding various materials made during a study and, ultimately, as a common ground for comparing films prepared in different laboratories. In the present study, we will be exploring the utility of this classification scheme and its extension to a-Si:H rf-sputtered films. A preprint of our paper describing the zone model as applied to a-Si is Appended.

EXPERIMENTAL RESULTS AND DISCUSSION

Film Preparation

During this first quarter, a series of films were prepared by rf-sputtering in which the partial pressure of hydrogen, P_H , was varied between 4×10^{-6} Torr and 10mTorr with the total pressure ($\text{Ar} + \text{H}_2$) constant at 20mTorr. Both the rf-power level and substrate-target distance were constant at 100W ($.8\text{W}/\text{cm}^2$) and 32mm, respectively. The films were prepared in an MRC system (Model 8502S) with a gas inlet system consisting of an MKS Baratron capacitance manometer, a Granville - Phillips closed-loop feedback controller and servo-controlled leak valve, mass flowmeters, and a Ti-getter Ar purifier. The diffusion-pumped system is routinely pumped to 5×10^{-7} Torr before throttling and backfilling

with the sputtering gas. The sputtering target is a 5" diameter by 1/4" thick polycrystalline Si disc (Specialty Metals, Inc.) of 99.9999% purity.

In each of the tests, various substrates were placed for use in the different structural, chemical, and physical investigations. During this stage of the study, our primary concern was establishing whether or not anisotropic etching occurs in a-Si:H films in a manner similar to that perviously found for a-Ge and a-Si and, if so, its nature.

Characterization

1. Etching Behavior. Although the etching behavior varied with the P_H during sputtering and was qualitatively different that the etching of undoped a-Si films, anisotropic etchants were found for all the various films. A number of etchants were studied:

HF:HNO₃:H₂O at RT

HF:HNO₃:HAc:H₂O: at RT

49%HF at RT

HCL at RT

20% NaOH at 90°C

30% KOH at 90°C

Na₂O₂ at RT

The second etchant is the most succesful in general although the caustic etchants have limited success. There is a definite trend that the etchant reactivity decreases with increasing P_H .

2. Reflectivity. Total reflectance measurements (Beckman DK-2A) were made in the wavelength range 220 to 2500nm with an integrating sphere and BaSO₄ standard. Due to the increase of the band gap with hydrogenation of a-Si, the films (~5 - 10μm thick) are somewhat transparent in the measurement range, especially in the near IR, and

thus, contributions due to reflection off the back surface have to be accounted for. Considering these corrections we have obtained textured a-Si:H films with a total surface reflectance of less than 3%. The microstructure of this particular ($P_H = 1.5 \times 10^{-4}$ Torr) is shown in the next section.

3. Microstructure. As discussed above the etched film microstructure not only finds utility in a drastically decreased solar reflectance loss but also as a convenient method of classifying variously prepared a-Si:H films in terms of the structure zone model. Our preliminary results show that the undoped a-Si (Fig. 1 of Appendix) and doped a-Si:H films (Figs. 1 and 2) have similar but yet different etched microstructures. It appears that secondary nucleation effects are occurring in the hydrogenated films and in varying degrees with P_H (compare Fig. 1a and Fig. 2a). Note, for instance, the modular growth (Fig. 2c) and the flaky nature (Fig. 2x and b) in the film prepared at $P_H = 1.5 \times 10^{-4}$ Torr. As seen in Fig. 1d and Fig. 2c the unetched surfaces show some microstructure which is related to the resulting etched film microstructure, although the fractured edges give no such indication (note conchoidal fracturing).
4. Characterization of a-Si:H Films Using the SIPS Technique. The a-Si:H films prepared under different rf-sputtering conditions were analysed using the Sputter-Induced Photon Spectrometry (SIPS) technique. In SIPS, we bombard the sample surface with an Ar^+ ion beam and we detect the light emitted as a result of the de-excitation of neutral sputtered atoms leaving the surface in excited states. Since ion-beam sputtering results in the gradual removal of the atomic layers on the surface, one can measure the concentration-versus-depth profile of any constituent element in the solid by simply monitoring

the intensity of the appropriate spectral line as a function of time. In the a-Si:H films, we are mainly interested in the elements H and Si and they are detected by measuring the intensity of the H6563Å and Si2882Å lines.

In our SIPS experimental set-up, we can monitor both the H6563Å line and the Si2882Å line simultaneously as a function of time so that any variation of concentration with depth, due to inhomogeneity or density changes in the films, can be detected.

In order to quantify the amount of H in the films, we have made a request to Dr. C. W. Magee of RCA Laboratories to provide us with 3 or 4 a-Si:H films with known H concentrations. It is hoped that we can then construct a working curve from these standards to determine the H/Si concentration ratios of the unknown rf-sputtered films which we prepared. So far, however, we have only received one such standard, but we shall receive more in the near future.

The initial a-Si:H films that we prepared were about 2000Å thick and these were deposited on stainless steel and copper substrates. These films yielded interesting Si and H depth profiles, each of them showing a distinctly sharp interface between the film and the substrate. One problem associated with H analysis is the hydrogen background in our vacuum system which has a base pressure of 1×10^{-7} torr. We are presently constructing a new SIPS unit with an ultra-high vacuum (1×10^{-10}) target chamber which will become operational in October 1979. Despite the high H background, this initial batch of films did not present any problem as the H signal in the film was several times above the background.

The second batch of a-Si:H films were considerably thicker, with thicknesses ranging up from 5 to 10µm. These films presented some

some problems as the depth-profiling process with the ion beam took a very long time, (several hours in fact) and no sharp transition was observed, due to a cratering effect, at the interface between the film and substrate. From our data we conclude that to carry out a meaningful analysis of the films, we should limit ourselves to films with thickness $\leq 1\mu\text{m}$. The next phase of the characterization experiments with SIPS will consist mainly of quantifying the H content on $\sim 1\mu\text{m}$ thick films by comparison with standards (or from a working curve).

WORK IN PROGRESS

The next series of tests have been started in which the total sputtering gas pressure is being varied. There are several reasons for this choice. First, we have been shown previously⁽⁹⁾ that P_{tot} has a large effect on macroscopic film stress (and thus mechanical stability both before and during etching), argon and oxygen content, and film density. Second, at higher gas pressures energetic particle bombardment of the growing film decreases due to thermalization by scattering. In A-15, Nb_3Ge superconducting films it was found that T_c was maximized (23.4K) at high sputtering gas pressures due to, primarily an increase in crystal lattice perfection (directly related to reduction in film bombardment damage).⁽¹⁰⁾

Two other sputtering systems are currently being made operational. In one system, the chamber can be pumped to UHV ($\sim 10^{-9}$ Torr) before admitting the sputtering gas and thus will allow us to study the effect of low levels of oxygen incorporated during the sputter-deposition process. The second system will allow us to sputter with toxic (e.g. arsine, diborane, phosphine) and corrosive (e.g. SiH_4 , SiF_4 , F) gases.

Physical property measurements in progress include IR and Raman spectroscopy, optical absorption, photoluminescence conductivity, and photoconductivity. Devices and device property measurements are being planned.

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Fig. 1 SEM micrographs of the top surface and fractured edge of an a-Si:H film after (a-c) and before (d-f) etching. The film was prepared at 100W ($0.8\text{W}/\text{cm}^2$), $P_{\text{tot}} = 20 \times 10^{-3}\text{Torr}$, and $P_{\text{H}} = 6.5 \times 10^{-4}\text{Torr}$.

Fig. 2 SEM micrographs of the top surface and fractured edges of an a-Si:H film after (a,b) and before (c,d) etching. The film was prepared at 100W ($0.8\text{W}/\text{cm}^2$), $P_{\text{tot}} = 20 \times 10^{-3}\text{Torr}$, and $P_{\text{H}} = 1.5 \times 10^{-4}\text{Torr}$.

APPENDIX

Black a-Si Solar Selective Absorber Surfaces

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ABSTRACT

Amorphous Si films display a unique anisotropic etching phenomenon in which a columnar microstructure results. The alignment of the anisotropic microstructure is related to the average angle of the depositing material. Since cross-sectional spacing of the columns is less than the wavelength of light, a continuous grading of the refractive index occurs and results in a drastic reduction in the total reflectance from 40-50% in the as deposited film to <2% in the etched film. The etchant, HF/HNO₃, apparently oxidizes rapidly down aligned void networks followed by an equally rapid dissolution and removal step. Such a semiconductor film on a low IR emissivity metallic substrate is a potentially efficient photothermal selective absorber surface.

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A good photothermal selective absorber surface must have low reflectance and high absorptance throughout the solar spectrum and low emissivity in the IR black body radiation region. A semiconductor has high visible absorptivity and, when deposited on appropriate metal substrates, low effective IR emissivity. However, due to its high refractive index the visible reflectance is around 50% for most semiconductors. The three general approaches to reducing this high reflectivity are discontinuous, stepped, grading of the refractive index (anti-reflection coatings), effective lowering of the refractive index (semiconductor/insulator cermet films), and continuously grading the refractive index (rough surface).

This latter approach was first used in reducing the reflectivity of crystalline Si solar cells (from 40% to 50%) by etching single crystal surfaces preferentially along certain crystal planes.^(1,2) Recently it has been found that single crystals of GaAs can be etched to reveal a columnar structure with sizes on the order of the wavelength of light.⁽³⁾ This same type of sub-micron columnar microstructure was first observed for amorphous Ge (a-Ge) sputtered films⁽⁴⁾ in which preferential etching apparently proceeds along anisotropic microscopic voids in these materials and results in a drastic lowering of the reflectance from ~50% to less than 2%. The only other reports of surface-structural control of reflectivity for selective absorber applications is that of electro-deposited Ni⁽⁵⁾ and W⁽⁶⁾.

Stephens and Cody⁽⁷⁾ have established that an ideal continuously graded absorber should have dimensions in the plane of the film surface on the order of, or less than, the wavelength of light and a grading depth of at least one-quarter of the wavelength of the light absorbed. The black Ge⁽⁴⁾ and etched GaAs⁽³⁾ fulfill these requirements while the dendritic Ni and W^(5,6) have larger-sized surface microstructures which are not as efficient since reflectivity

is decreased through a multiple reflection mechanism rather than a grading of the refractive index. In this communication, we describe the anisotropic etching phenomenon of a-Si thin films which, when etched in an HF/HNO₃ solution, reveal a columnar microstructure similar to that for a-Ge⁽⁴⁾.

The a-Si films were prepared by rf-sputtering in an MRC Model SES 8632 system from a 44 mm diameter hot-pressed Si target. The substrates were glass microscope slides. A series of a-Si films were prepared with gas pressure (10-50 x 10⁻³ Torr) and rf-power (50-200 watts) independently varied. The substrate-to-target distance was constant at 32 mm. The post-deposition anisotropic etching behavior was found to vary with preparation conditions as has been found for other properties of a-Si⁽⁸⁾ and the analogous a-Ge⁽⁹⁾ films. We report here detailed results on films prepared at two different power levels (50 and 200 watts) with the gas pressure constant at 30 x 10⁻³ Torr.

The anisotropic etchant, HF/HNO₃, for the a-Si films apparently acts in a similar manner to the H₂O₂ etchant for a-Ge⁽⁴⁾ films. While the H₂O₂ acts as both an oxidant and dissolution agent for a-Ge, for the a-Si films the HNO₃ is the oxidant and the HF dissolves the resulting SiO₂ layer. In both cases no limiting reaction barrier occurs; a 20 μm thick a-Si films etched completely in approximately 10 seconds leaving a highly aligned needle-like microstructure (see Fig. 1). Both the "needle" size and spacing are below 1 μm and similar to the idealized structure of Stephens and Cody.⁽⁷⁾ The resulting decrease in total reflectance between the unetched and etched a-Si film is seen in Fig. 2. The etched film appears flat black since this low reflectivity (<2%) is maintained for viewing angles of <45° from normal incidence.

A series of SEM micrographs (Fig. 3a) of fractured edges of an etched a-Si film (black Si) as a function of radial distance from the center of the

glass substrate show that the angle of the columnar structure (column size $\sim 2000\text{\AA}$ diameter) with respect to the substrate (Fig. 3b) varies in the same manner as the thickness distribution with radial distance. From geometrical considerations based upon the distributed nature of the sputtering source and an ideal cosine emission of material from all points on the source, it is reasonable that the columnar direction is directly related to the average angle of the depositing vapor flux at the substrate. Shaldervan and Nakhodkin⁽¹⁰⁾ have shown similar behavior in evaporated amorphous Ge films, although their column size was determined to be 30-70 $\text{\AA}$ in diameter by transmission electron microscopy. Similarly, this microstructural angular dependence has been seen in polycrystalline films of Al, Au, Ag, Cr, Bi, Te, and CdTe^(11,12). Several mechanisms have been put forth to explain this columnar microstructure: self shadowing⁽¹¹⁾, oxygen incorporation hindering lateral grain growth⁽¹¹⁾ and recrystallization due to high surface mobility^(11,12), the latter mechanism occurring only in polycrystalline films.

The anisotropic, columnar microstructure of crystalline thin films is well documented⁽¹³⁾. Movchan and Demchishin⁽¹³⁾ were the first to classify the various microstructures of evaporated films into three distinct zones as a function of T/T_m where T is the film temperature during preparation and T_m is the melting point of the particular material. Thornton⁽¹⁵⁾ extended this structure zone model to sputtered crystalline metal films by adding another parameter (sputtering gas pressure) to the model and establishing a fourth zone (Zone T). Although little work has been reported on the microstructure of amorphous films, the zone model apparently still applies⁽¹³⁾ for the first two zones (Zone 1 and Zone T) while Zones 1 and 3 apply only to crystalline films. Recently, we have shown that the etching behavior in a-Ge sputtered

films⁽⁴⁾ is useful in revealing their anisotropic microstructure and thus their applicability to and location in the structural zones⁽¹⁶⁾. It was concluded that the etching revealed two distinctly different types of columns, designated as macrocolumns ($\sim 2\text{-}10\mu\text{m}$ dia) and columns ($\sim 0.1\text{-}0.5\mu\text{m}$ dia) which corresponded to Zone I and Zone T structures, respectively. Further, we have now shown by both TEM and FIM⁽¹⁷⁾ that in a-Ge films there is a third, even smaller columnar structure (microcolumns) with dimensions similar to those reported by Shaldervan and Nakhodkin⁽¹⁰⁾. Thus, the complete picture appears to be that macrocolumns are comprised of bundles of columns which, in turn, are made up of bundles of microcolumns with macrovoids, voids, and microvoids (or low density regions) surrounding these corresponding microstructural elements⁽¹⁶⁾.

In this study we have clearly revealed the columns ($\sim 2000\text{\AA}$ dia.) in a-Si sputtered films (see Fig. 1) which correspond to a Zone T structure in the zone model. As found for a-Ge⁽¹⁶⁾, these films were deposited on atomically smooth glass slides. The microcolumnar nature of a-Si films has been shown previously by phase contrast TEM techniques⁽¹⁸⁾ and small angle x-ray scattering to be similar to that found for a-Ge⁽¹⁹⁾. Thus, it is not surprising that the a-Si microstructure can also be classified in terms of the structure zone models. Although macrocolumns have not yet been demonstrated, it is expected that a-Si films deposited onto rough substrates will be macrocolumnar (Zone I), analogous to a-Ge⁽¹⁶⁾. An important question that remains concerns the size of the etched columns: a-Si (and a-Ge) films are composed of an apparently uniform array of aligned microcolumns separated by an interconnected grid of honeycomb-like microvoids, yet the black Si (and black Ge) etched columns are about an order of magnitude larger in diameter. Although not providing a direct answer there are two experimental

observations of related phenomena which are noted. First, a-Ge films show a unique "explosive" crystallization phenomenon⁽²⁰⁻²²⁾ in which 1000-2000Å crystallites form within 10^{-7} sec. Second, TEM samples of a-Ge, which show the typical structure of microvoids separating 100-200Å microcolumns, under certain beam conditions crystallize spontaneously resulting in, again, 1000-2000Å single crystals⁽²³⁾. In both cases, the crystallite size is essentially the same as the etched column size.

In conclusion, it is apparent that the anisotropic etching phenomenon we are reporting is due to rapid etching down aligned void networks followed by a slower, more normal etch rate perpendicular to the void surface. The voids, or low density regions, and columns are highly aligned over rather large distances ($>20\mu\text{m}$) with the alignment in the direction of the impinging vapor species. The film microstructures can be classified by the structure zone model.

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Fig. 1 SEM micrographs of the top surface (a) and fractured edge (b) of an HF/HNO₃ etched a-Si film.

Fig. 2 Total reflectance (specular plus diffuse) for an as-deposited a-Si film (1) and an etched, black Si film (2) from the uv to the near-IR. Several other black absorbers are given for comparison.

Fig. 3a SEM micrographs of the fractured edge of an etched a-Si film as a function of radial distance (R) from the center of the film. The pictures were taken perpendicular to the fractured edge and at a 45° tilt.

Fig. 3b Angle of the aligned microstructure with respect to the substrate (lower black portion of each micrograph) as a function of radial distance.

FIGURE 1

FIGURE 2

FIGURE 3a

FIGURE 3b