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**AMORPHOUS THIN FILMS
FOR
SOLAR CELL APPLICATION**

Quarterly Report No. 3
For Period
October 1, 1979 - December 31, 1979
LMSC-D678918

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A. D. Jonath
K. M. Monahan
J. L. Crowley
H. F. MacMillan

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Section 1

INTRODUCTION

The identification, content, and role of impurities in a-Si thin films are sources of speculation not only for possible device performance degradation but also for their impact on film-property diagnosis. This concern is presently shared by those using all deposition processes, with oxygen and argon receiving attention as the most commonly introduced impurities. Oxygen to some degree (and with nitrogen) might have beneficial effects on film photoconductivity (Ref. 1); yet device performance is said to suffer when oxygen concentration approaches one percent (Ref. 2). Argon inclusion effects on film structure (Ref. 3), resulting post-deposition oxidation (Ref. 4), and the nature of the defect state (Ref. 4) are indicated but unclear.

In our work this quarter, we emphasized (1) the measurement of oxygen concentration profiles through the film using Rutherford backscattering and nuclear reaction methods; and (2) the control over oxygen inclusion in the sputtered films. The first is discussed in Section 2. Depositions are summarized in Section 3.

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Section 2

0000 NUCLEAR REACTION AND RUTHERFORD BACKSCATTERING ANALYSIS
OF OXYGEN AND ARGON IN a-Si FILMS

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Considerable effort in this quarter was directed toward converting relative oxygen concentration profiles to absolute measurements. This conversion was achieved by calibrating the nuclear reaction analysis (NRA) system against stoichiometric SiO₂ standards.

In addition, relative argon concentration profiles were obtained using the Rutherford backscattering technique (RBS). We expect to convert these to absolute measurements in the next quarter.

2.1 OXYGEN PROFILES BY NRA – INTRODUCTION

The importance of oxygen as an active contaminant that can modify the electrical characteristics of sputtered (Refs. 5 and 6) and plasma-deposited (Ref. 7) a-Si films has been well established. Unfortunately, conventional methods for determining oxygen concentrations in a-Si films, such as electron microprobe analysis (EMA) or Fourier transform infrared spectroscopy (FTIR), at best yield concentrations averaged over the depth of the material. For FTIR, oxygen present in other than Si-O bond states might not be observed. Secondary ion mass spectroscopy (SIMS), which normally yields impurity concentrations as a function of depth, is impractical for a-Si films because of either the high reactivity of Si with background oxygen (Ref. 8) or the difficulty of obtaining an absolute calibration (Refs. 7 and 9). We have chosen to use resonant nuclear reaction analysis (NRA) for the current work since this technique has the two advantages of being nondestructive and of yielding accurate oxygen profiles.

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2.2 OXYGEN PROFILES BY NRA – METHOD

To detect oxygen, the $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ nuclear resonance reaction at 3.045 MeV was used. This process, by which alpha particles incident on the ^{16}O nucleus produce the short-lived $^{20}\text{Ne}^*$ compound nucleus in its 7.17-MeV excited state, is described by Eq. (1):

The subsequent decay to ^{16}O produces an alpha particle having ~ 65 percent less kinetic energy than the incident alpha particle, the loss being taken up by recoil of the ^{16}O nucleus.

The narrow resonance width (~ 10 keV) of the reaction in Eq. (1) allows the oxygen concentration to be measured as a function of depth in thin-film samples. As the incident alpha particle penetrates the film, it loses energy due to small angle scattering at a known rate, dE/dx . Thus, by increasing the incident alpha energy E_α in intervals of 10 keV, it is possible to produce the $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ resonance reaction in progressively deeper regions of the film. The depth of the sampled region is given by:

$$X = (E_\alpha - 3.045 \text{ MeV}) / (dE/dx) \quad (2)$$

For a 10-keV resonance width and a silicon $dE/dx = 200 \text{ keV}/\mu\text{m}$, the depth resolution is approximately $500 \text{ \AA}$. By calibrating the detection system with a sample of known oxygen content and depth profile (typically, stoichiometric SiO_2), it is possible to measure concentrations as low as a few tenths of an atomic percent.

2.3 OXYGEN PROFILES BY NRA – CALIBRATION

The $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ resonance at 3.045 MeV can be profiled with a thin $0.035\text{-}\mu\text{m}$ SiO_2 sample on a (100) channeled, crystalline silicon substrate. The incident alpha energy is gradually increased in small increments from 2.8 to 3.2 MeV. At each energy, the integrated resonant alpha yield in the film is measured and plotted as a function of energy, as in Fig. 1. The resolution of the profile is limited by the

Fig. 1 The ${}^{16}\text{O}(\alpha, \alpha){}^{16}\text{O}$ Resonance Line Profile Determined From a 35-nm-thick SiO_2 Film

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thickness of the SiO_2 film; in this case, the $0.035\text{-}\mu\text{m}$ resolution limit is less than the inherent $0.050\text{-}\mu\text{m}$ limit due to the width of the resonance. It should be noted that the alpha yield does not fall to zero far from the resonance. In fact, the low-energy "tail" in Fig. 1 can be a source of considerable error. If it is not taken into account in the data analysis, the resulting oxygen profiles will have an anomalous decrease in resolution near the front surface of the sample.

In order to calibrate oxygen profiles in the relatively thick a-Si samples, we have determined the maximum alpha yield at resonance for eight SiO_2 films of various thicknesses up to $1.950\text{-}\mu\text{m}$. The results are plotted as a function of SiO_2 thickness in Fig. 2. The yield curve appears to increase nearly linearly until the SiO_2 thickness becomes comparable to the $0.050\text{-}\mu\text{m}$ resolution due to the nuclear resonance width in the material. At this point, the curve begins to bend and saturate at a constant value for the thicker films. It is this saturation yield that corresponds to an SiO_n sample with an oxygen content of 67 atomic percent ($n = 2$). The SiO_2 samples have been verified by electron microprobe analysis to be stoichiometric, i.e., to have an oxygen concentration of 65 ± 2 atomic percent. The SiO_n content of a-Si films can be determined by iteration from the yield ratio in Eq. (3) below:

$$Y = nE'(n) \rho(n) / 2A(n), \quad (3)$$

Where Y is the ratio of the SiO_n yield to the SiO_2 yield, n can vary from zero to two, $E'(n)$ is the ratio of dE/dx of SiO_n to SiO_2 , $\rho(n)$ is the ratio of the density of SiO_n to SiO_2 , and $A(n)$ is the ratio of the molecular weight of SiO_n to SiO_2 . For the first iteration, $E'(n_1)$ and $\rho(n_1)$ are set equal to unity and $A(n_1) \equiv A(0)$ so that

$$n_1 = 2A(0)Y \quad (4)$$

Successive approximations are obtained from

$$n_{j+1} = 2A(n_j)Y / \rho(n_j)E'(n_j) \quad (5)$$

In practice, the series converges so rapidly that n_2 is adequate to obtain absolute concentrations to within one atomic percent.

Fig. 2 Oxygen Calibration Curve Derived From Profiles of Stoichiometric SiO₂ Films of Various Thicknesses

2.4 OXYGEN PROFILES BY NRA - SAMPLE PREPARATION

Hydrogenated a-Si films were prepared for NRA by dc sputtering with argon in a planar magnetron system using hydrogen as the reactive gas. N-type single-crystal silicon ($0.2 \Omega\text{-cm}$) containing 10^{17} cm^{-3} arsenic was used for the target cathodes. The deposition conditions for two samples with low and high hydrogen content are listed in Table 1. The single-crystal Si substrates were mounted in a rotating carousel resulting in a deposition duty cycle of approximately 5 percent. Thus, although the sputtering rate was estimated to be 250 nm/min , the actual deposition rate (measured by film thickness divided by deposition time) ranged from 12 to 14 nm/min for the samples in Table 1.

Table 1. DEPOSITION PARAMETERS FOR TWO a-Si FILMS

Sample No.	84	95
H partial pressure (mtorr)	0.6	2.5
Ar partial pressure (mtorr)	1.7	1.7
Deposition rate (nm/min)	12	14
Film thickness (nm)	430 ± 50	500 ± 50
Substrate temp. ($^{\circ}\text{C}$)	~ 100	~ 100
Target power (W)	1080	1080

2.5 OXYGEN PROFILES BY NRA - RESULTS

The detected alpha energy distribution from sample 84 is shown in Fig. 3. An $^{16}\text{O}(\alpha, \alpha)^{16}\text{O}$ resonance peak sits atop the RBS spectrum of a-Si on its c-Si substrate. From the dE/dx value for Si, one can determine the approximate thickness of the a-Si film; in this case, $0.49 \pm 0.05 \mu\text{m}$. Note also the 10 percent reduction in silicon density in a-Si as compared with the single-crystal Si substrate. Part of this reduction is ascribed to oxygen incorporation during deposition. The amount of hydrogen incorporation is also considered to affect the density (Ref. 10). The oxygen resonance peak is located at significantly lower detected alpha energy because of the large kinetic energy transfer from the incident alpha particles to the recoiling oxygen nuclei.

Fig. 3 Rutherford Backscattering Spectrum of a-Si Film (Sample No. 84)
Showing Superimposed Oxygen Resonance Peak ($E_{\alpha}(\text{inc.}) = 3.13 \text{ MeV}$)

By integrating the area under the resonance peak for a series of incident alpha energies, one may assemble a profile of oxygen concentration in an a-Si film, as shown in Fig. 4 for sample 84. The sampling depth (top scale) is calculated from dE/dx values for alpha particles entering Si at 3.1 MeV and leaving at 1.1 MeV. The scale should be considered accurate to within 10 percent. Zero represents the vacuum/a-Si interface; and 0.5- μm , the approximate a-Si/c-Si interface. The striking feature of this profile is the high oxygen concentration in that portion of the film produced in the first fifteen minutes of deposition. This profile is direct evidence of strong gettering of oxygen by Si atoms during the deposition of a-Si films.

A refinement of the technique for integrating under the oxygen resonance peaks, taking into account the low-energy tail of the resonance, resulted in the profile shown in Fig. 5 for sample 95. Again, there is confirming evidence for strong oxygen gettering by Si during the initial stages of deposition. Note, however, that the leading edge of the profile (the vacuum/a-Si interface) is much sharper than that of Fig. 4. Optical and scanning electron micrography indicate that the sharp leading edge is the result of refined data analysis rather than a dissimilarity in either surface roughness or porosity of the two films. The difference in the hydrogen partial pressure during deposition of the two films does not seem to affect oxygen incorporation appreciably.

2.6 ARGON PROFILES BY RBS - RESULTS

Although Rutherford backscattering (RBS) cross sections are relatively small compared with nuclear resonance cross sections, it is frequently possible to profile concentrations of elements with atomic weights greater than that of Si. The backscattered alpha energies from these heavier elements will be higher than those from silicon. Even a small number of counts are detectable if they occupy a part of the detected alpha energy spectrum that does not overlap the Si RBS background. A higher-energy portion of the spectrum (cf. Fig. 3) is magnified in Fig. 6 showing the Ar profile. The high-energy shoulder on the Si edge is due to ^{29}Si (and ^{30}Si). The high-energy edge for ^{28}Si , the common isotope, is more than two orders of magnitude greater than this. A rough calculation of the Ar concentration relative to Si yields a value of 0.1 - 0.2 atomic percent. Electron microprobe studies indicate that argon

Fig. 4 Oxygen Concentration Profile of a-Si Sample No. 84

Fig. 4 Oxygen Concentration Profile of a-Si Sample No. 95

concentrations are about 0.25 percent in these films. The profiles of Ar as a function of depth show a uniform distribution in both samples. As one might expect, argon does not appear to be strongly gettered by silicon.

2.7 CONCLUSIONS

The most significant result of the oxygen profiling studies in a-Si is the observation of strong gettering by Si atoms. Since oxygen is known to be an electrically active impurity in a-Si films, it will be necessary to guard against incidental incorporation of oxygen into the films. (Controlled oxygen incorporation will always be possible by introducing a variable leak into an oxygen-free vacuum system.) The most likely source of incidental oxygen in 10^{-6} to 10^{-7} -torr vacuum systems is water vapor. This source can be significantly reduced by Meisner trapping, vacuum interlocks, increased pumpdown times, and/or mild bakeout of the vacuum chamber.

To study profiles of impurities other than oxygen and with atomic weights equal to or greater than that of Ar, standard RBS techniques appear to be satisfactory; at least, to an accuracy of 0.1 atomic percent. In samples 84 and 95 there were indications of other high-mass impurities such as arsenic and possibly molybdenum. Profiles of these elements, also, may prove important in explaining the electrical activity of hydrogenated a-Si films.

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Section 3

GROWTH AND DOPING OF AMORPHOUS THIN FILMS

The descriptions of the three sputter deposition systems playing roles in this program were presented in the First Quarterly Report (Ref. 11). They are (1) a low-cost planar magnetron (PM) prototype system at Sputtered Films, Inc. (SFI), Santa Barbara, California, for all preliminary and feasibility-study a-Si:H depositions, (2) an LMSC-funded PM system using SFI Research S-guns but with widespread design improvements based on program needs and experience with the SFI prototype system, and (3) a cylindrical magnetron (CM) system at Telic Corporation to verify the potential for scaling up the deposition parameters in order to achieve quality in large-area films.

During this quarter, the cylindrical magnetron (CM) system at Telic Corporation has been brought online to deposit a-Si films at different substrate temperatures and argon partial pressures. The depositions were accomplished using the transmutation-doped polycrystalline silicon cathode. The CM system was operated in the dc mode, which greatly simplified the cathode and chamber design. Before dc operation was verified, the design problems involved in operating an rf cathode were identified and solved.

The CM chamber was modified so that films could be deposited on four substrate locations simultaneously. One substrate position is unheated; the other three positions can be heated to temperatures in excess of 400°C. Provisions have also been made in the chamber to measure the conductivity of the films immediately after deposition but before the chamber is let up to atmosphere to determine if oxygen absorption after deposition causes a degradation in electrical properties.

Amorphous silicon films without intentional hydrogen incorporation were deposited at argon partial pressures of 1 to 30 mtorr. The stress in the films changes from compressive at 1 mtorr to tensile at 10 mtorr and greater, with the films deposited

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at 5 mtorr being virtually stress-free. Films deposited at these various argon partial pressures were deposited on substrates of 200°C, 300°C, and 400°C and on unheated substrates. The electrical properties of these films are similar to those of films deposited in the prototype planar magnetron system.

The gettering of oxygen seen in the results of the previous section is considered a possible control over oxygen inclusion into the films. Depositions were performed in the prototype PM at SFI to compare oxygen gettering in long- and short-presputter pumpdown cycles with the increased gettering capability (deposition area) of the CM system at Telic. The resultant films are being analyzed.

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Page No.

Page No.

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