DEPOSITION OF A-SiC:H, A-SiO₂, AND TETRAHEDRAL-C
WITH PROGRAMMABLE *IN-SITU* ETCHING

FINAL PERFORMANCE REPORT

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DEPOSITION OF A-(Si/C):H AND A-(Si/Ge): THIN FILMS REMOTE PLASMA ENHANCED CVD AND PROGRAMMABLE IN SITU ETCHING

I. INTRODUCTION

This research program was originally defined to investigate the deposition of semiconductor and dielectric thin films using a low pressure remote plasma chemical vapor deposition system incorporating a process for etching the films. This etching was to be performed in a periodic fashion during the deposition process to remove defect regions in the film being deposited. The goal was to remove voids and other defects which are characteristic of low temperature deposition processes.

While the original research proposal suggested that the studies include the amorphous alloys (Si/C):H and (Si/Ge):H, subsequent funding reductions limited the work to the deposition of an amorphous silicon alloy material (a-Si:H). Intrinsic and doped forms of these materials have applications in the fabrication of single and multi-junction thin film solar cells.

II. ALLOY DEPOSITION SYSTEM

The remote plasma enhanced chemical vapor deposition (RPECVD) system was constructed utilizing standard vacuum system components wherever possible. A 3-inch OD 6-way stainless steel cross was the basis for the deposition chamber. A 29-mm ID quartz tube was connected to the chamber for the introduction of a helium/argon/hydrogen plasma. The plasma was created with a 13.6 MHz RF generator coupled to the plasma tube with an external coil. Deposition substrates were clamped to a heated stage located approximately at the center of the chamber. This stage can be heated to 300 °C. A 10% silane in helium mixture was injected from a dispersal ring spaced about 5 cm in front of the substrate surface. The deposition chamber is shown schematically in Fig. 1.

The high vacuum system consisted of a turbomolecular pump/rotary vane pump connected to the chamber through a gate valve. An ionization pressure gauge and quadrupole residual gas analyzer were also connected to the chamber through a high vacuum isolation valve. This system was used to pump and bake out the chamber after loading a substrate. After an overnight bake-out, the chamber pressure was in the mid- 10^{-8} Torr range. During the deposition cycle, a chemically resistant rotary vane vacuum pump was connected to the chamber through a throttle valve which was controlled by a capacitance pressure transducer. The pumping capacity of this throttling system was about 100 cm³/min at a chamber pressure of 250 mT.

The unique feature of this research program was to be the periodic etching of the deposited film during the deposition process. Initially, xenon difluoride was to be used as the Si etchant. However, it was indicated that the purity of available XeF₂ was not suitable for the deposition of high quality a-Si:H layers. Residual oxygen and water vapor can severely degrade the properties of undoped a-Si:H films. A high purity hydrogen gas source channel was provided

in order to permit the generation of a hydrogen plasma which slightly etches Si.

Fig. 1. Schematic representation of RPECVD deposition chamber.

Typical deposition conditions for the films were:

Substrate temperature	250 °C
RF power	22 to 29 watts
He flow rate (plasma)	80 sccm
10% SiH ₄ in He flow rate	20 sccm
H ₂ flow rate (plasma)	40 sccm
Chamber Pressure	250 mT

III. CHARACTERIZATION OF THIN FILMS

Cleaned Corning 7059 glass plates were used for the substrate material. After deposition the film thickness was measured with a stylus surface profiler. Subsequent electrical measurements were accomplished by photolithographically patterning a pair of parallel Al stripes deposited by electron beam evaporation. These stripes were 8 mm long with a separation of 1 mm. Probe contacts were made to these stripes for the measurement of photo- and dark conductivity in a high vacuum environment.

A Keithley Model 617 electrometer with a 25-volt bias source was used to determine the conductance of the coplanar electrode structures. These measurements were performed in a sputter ion pumped vacuum chamber with a typical pressure of 2×10^{-6} Torr. The samples were pre-annealed in this chamber for two hours at 180°C before measuring the electrical properties. This annealing established the as-grown dangling bond density and desorbed any surface gas species which might ambiguously affect the conductance behavior. The chamber had a Pyrex glass window for the illumination of the sample with a 1 kW ozone-free xenon lamp. A full spectrum exposure yielded an intensity at the sample surface of about 50 mW/cm^2 . Prolonged full spectrum exposure causes a degradation of the photo- and dark conductivity in the intrinsic a-Si:H thin films (the Staebler-Wronski effect). In order to monitor the light intensity during the exposure and photoconductance measurement sequences, a spectrally calibrated Si photodetector and narrow band optical interference filters were used. Typically, a 700 nm center wavelength filter was used, although photoconductance spectra were measured over the 500-800 nm range. By occasionally interrupting a prolonged full spectrum exposure, the xenon lamp power supply could be adjusted to maintain a relatively constant exposure intensity. Water cooling passages in the sample mounting block permitted control of the temperature at c. 25°C during the prolonged exposure process. This conductance characterization system is shown in Fig. 2.

Fig. 2. Photoconductance characterization system.

After light exposure degradation and electrical measurement the films were annealed for two hours at 180 °C. This heat treatment typically returned the photoconductance to about 70% of the as-grown pre-annealed value.

IV. THIN FILM CHARACTERISTICS

Examples of the characteristics of samples deposited under varying conditions are presented in Table 1. As a measure of comparison among the samples, the ratio of the photoconductance measured at 700 nm normalized with respect to the photon flux and the dark current, $G_{ph}/(F_{ph}I_d)$, is presented. Also shown is the conductance ratio after a two-hour exposure. Sample S1 is a reference sample, deposited with a continuous plasma excitation of silane. Samples S3 and S6 are examples of interspersing periods of hydrogen plasma with silane excitation. These latter "hydrogen plasma" samples appear to offer slightly less degradation in photoconductance after optical exposure. Variations in film thickness among the samples make accurate comparisons difficult. The spectral behavior of the photoconductance normalized with respect to the photon flux density is illustrated in Fig. 3 and 4 for the three samples. In Fig. 4 the annealed response is also shown for Sample S6. The time behavior the photoconductance degradation of Sample S6 with light exposure is presented in Fig. 5.

Table 1. Photoconductance Characteristics of Various a-Si:H Layers.
Deposition Parameters: Substrate Temperature = 250 °C,
RF Power = 26 watts, Chamber Pressure = 250 mT.

Sample No.	Thickness (μm)	Deposition Condition	$G_{ph}/(F_{ph}I_d)$ (@ 700 nm) (S-cm ² -s/photon)	$G_{ph,exp}/G_{ph,init.}$ (@ 700 nm) (2-hr exp.)
S1	1.4	3 hrs SiH ₄ (reference)	1.70×10^{-11}	0.027
S3	1.4	20 min. SiH ₄ , 10 min. H ₂ (9 cycles)	5.58×10^{-11}	0.072
S6	0.63	10 sec. SiH ₄ , 30 sec. H ₂ (360 cycles)	2.28×10^{-12}	0.043

V. CONCLUSIONS

In this research thin films of amorphous Si were deposited in a remote plasma enhanced deposition system with periodic interruptions of the silane flow to expose the film to a hydrogen plasma. Using the degradation of photoconductance with light exposure as a measure of film stability, Sample S3 (20 min. SiH₄, 10 min. H₂) had a two-hour exposure photoconductance degradation ratio of 0.072, the largest of the various films deposited. This ratio was somewhat more than twice that of Sample S1 deposited under continuous silane excitation conditions.

Fig. 3. Spectral photoconductance of Samples S1 and S3. Initial and two-hour exposure results are shown.

Fig. 4. Spectral photoconductance of Sample S6. Initial, two-hour exposure, and annealed states are shown.

Fig. 5. Time response of degradation of 700 nm photoconductivity during optical exposure of Sample S6.