

## ION-BEAM-HYDROGENATED AMORPHOUS SILICON

Y. S. Tsuo, X. J. Deng, Y. Xu, A. K. Barua<sup>\*</sup>, S. Asher and S. K. Deb  
Solar Energy Research Institute, Golden, Colorado 80401

<sup>\*</sup>Indian Association for the Cultivation of Science, Calcutta, India 700032

## ABSTRACT

A Kaufman ion-beam source has been used to study the rehydrogenation and postdeposition hydrogenation of amorphous silicon. In the rehydrogenation study, hydrogen atoms were implanted into glow-discharge-deposited amorphous silicon materials in which the hydrogen content had been driven out by heating. In the posthydrogenation study, amorphous silicon samples with no hydrogen content detectable by infrared absorption and no photoconductivity were used as the starting material. These materials were deposited by thermal CVD, magnetron sputtering, or RF glow discharge.

## INTRODUCTION

Most high-quality amorphous silicon hydrogen alloys (a-Si:H) are hydrogenated during deposition. For example, in the commonly used plasma-assisted chemical vapor deposition (CVD) (or glow discharge) a-Si:H deposition process [1], the main precursors in high-quality film deposition are believed to be the SiH<sub>3</sub> radicals. Processes of silicon-network building, hydrogen incorporation, and hydrogen elimination at the growing film's surface determine the deposited film's hydrogen content and bonding configurations. Methods of introducing hydrogen into amorphous silicon (a-Si) after deposition, independent of the deposition reaction chemistry, will likely permit more control of the hydrogen content and bonding configurations. Postdeposition hydrogenation (posthydrogenation) also provides more freedom to choose the methods and conditions of the amorphous silicon deposition. For example, high-temperature deposition or annealing can be used to improve the density and adhesion of a-Si before hydrogenation, and high-deposition-rate methods can be used for the a-Si deposition. Posthydrogenation techniques can also add flexibility in the development of new a-Si:H device structures and fabrication techniques. In addition, it has been reported [2-6] that posthydrogenated a-Si:H suffers much less light-induced degradation, known as the Staebler-Wronski effect [7], than conventionally deposited a-Si:H.

Studies reported in the literature on the posthydrogenation of undoped a-Si [8] have so far failed to produce a-Si:H films with photosensitivities comparable to those of conventional a-Si:H hydrogenated during deposition. The disadvantages of posthydrogenation techniques include non-uniform hydrogen depth profiles [9] and sputter-induced damages introduced during the posthydrogenation. Some possible reasons for the lack of success of posthydrogenation techniques also include insufficient hydrogenation, a poor a-Si starting material structure, and impurity contamination. The rehydrogenation process, first reported by Pankove [10], provides a means of testing the effectiveness of a posthydrogenation technique independent of the starting a-Si material structure and purity. In a rehydrogenation process, hydrogen atoms are reintroduced into an a-Si sample that had been hydrogenated during deposition and the hydrogen content subsequently driven out (dehydrogenated) by heating the sample to more than 500°C. The rehydrogenation results reported by Tsuo et al. [5] showed that a Kaufman ion-beam source can be used to efficiently introduce hydrogen into a-Si; the resulting Si-H bonds are mostly monohydrides. Recent results of our Kaufman ion-beam rehydrogenation and posthydrogenation of undoped a-Si are discussed in this paper.

## EXPERIMENTAL

The Kaufman ion-beam source used in our study has been described earlier [5]. It is a non-mass-analyzed ion source capable of generating a hydrogen ion beam with an ion-beam current density (J) up to about 2 mA/cm<sup>2</sup> and an ion-beam energy (E) up to 2000 eV. From previous studies [11,12] of hydrogen passivation of polycrystalline silicon grain boundaries, it is known that a Kaufman ion source is much more efficient than a radio-frequency (RF)-generated hydrogen plasma in introducing hydrogen atoms into polycrystalline silicon, because of the greater ion-beam current density and ion energy of the Kaufman ion-beam source. We have performed rehydrogenation studies of a-Si:H similar to that reported in ref. 5, using RF-generated hydrogen plasma instead of a Kaufman ion beam, and found that this is also true for a-Si. In the RF-plasma hydrogenation study, we used a pure hydrogen gas at a pressure of 4 Torr, a flow rate of 20 sccm, and a RF power density of 0.12 W/cm<sup>2</sup>. After 16 hours of RF-plasma hydrogenation at a sample temperature of 250°C, only about 2 at.% hydrogen was introduced into a dehydrogenated a-Si sample. Such a hydrogenation level can be achieved in only about 20 min, using a Kaufman ion beam with E = 600 eV and J = 1 mA/cm<sup>2</sup>. We believe the RF hydrogenation is inefficient because it is difficult for the low-energy hydrogen ions and radicals generated by the RF plasma to penetrate the surface oxide layer. This surface oxide layer on a-Si is produced when the a-Si sample is exposed to air.

For most ion-beam hydrogenation experiments, we used a-Si samples about 500 nm thick, deposited and processed in sets of two. One in each set was deposited on a Corning 7059 glass substrate and one on a high-resistivity crystalline silicon substrate, as described in ref. 5. The sample preparation procedures used for our rehydrogenation studies are similar to those reported in ref. 5. Three different deposition processes were used to prepare a-Si samples for posthydrogenation: thermal CVD, magnetron sputtering, and RF glow discharge. For the thermal CVD, we used a pure silane gas with a pressure of 5 Torr, a flow rate of 50 to 70 sccm, and a substrate temperature of 500° to 600°C. For the magnetron-sputtered a-Si, we used the system described in ref. 13 with an Ar sputtering-gas pressure of 2 mTorr, a RF power density of 1.2 W/cm<sup>2</sup>, and a substrate temperature of 180°C. The room-temperature dark conductivity of the undoped, magnetron-sputtered a-Si was  $4 \times 10^{-6}$  ohm-cm<sup>-1</sup>. There was practically no photoconductivity. The optical bandgap was 1.4 eV, as measured by the Tauc plot [5]. The dark-conductivity activation energy was 0.6 eV. The RF-glow-discharge-deposited a-Si samples were deposited at a substrate temperature of 480°C, using a pure silane gas pressure of 700 mTorr, a flow rate of 70 sccm, and a RF power density of 23 mW/cm<sup>2</sup>. No silicon-hydrogen bonds were detected in these a-Si samples by infrared absorption measurements. The room-temperature dark conductivity was  $5 \times 10^{-8}$  ohm-cm<sup>-1</sup> and the optical bandgap was 1.57 eV.

## RESULTS AND DISCUSSION

### Rehydrogenation

The Kaufman ion-beam source used in our study has an extractor grid diameter of 10 cm. The ion beam can be focused to an area roughly 5 cm in diameter at the sample stage to increase the ion-beam current density. The sputter rate for a-Si reported in Tsuo et al. [5] is for a focused ion beam with a current density around 1 mA/cm<sup>2</sup>. (The sputter-rate unit for Fig. 2 in ref. 5 was mislabeled; it should be in Å/min.) We have found that this sputter rate can be significantly reduced by using an unfocused ion beam. Fig. 1 shows the sputter rate for a-Si as a function of hydro-

gen ion-beam with  $J = 1 \text{ mA/cm}^2$  (curve A) and an unfocused ion beam with  $J = 0.3 \text{ mA/cm}^2$  (curve B). Lower current density increases the hydrogenation treatment time. For example, at a 600 eV ion-beam energy, a rehydrogenation treatment of  $0.2 \text{ mA/cm}^2$  for five hours produced about the same effect as a treatment of  $1 \text{ mA/cm}^2$  for one hour, but only about 30 nm of the material thickness was removed, instead of around 100 nm of material removal with the  $1\text{-mA/cm}^2$  beam. The difference in the material-removal rate for different ion-beam current densities is probably due not only to the difference in the physical-sputtering rate but also to the difference in the rate of chemical etching of a-Si by the hydrogen ions. Although the hydrogenation treatment time depends on the ion-beam current density and energy, we found that the resulting a-Si:H material quality is relatively independent of these variables as long as the desired hydrogen content is reached and the ion-beam energy is higher than about 400 eV.

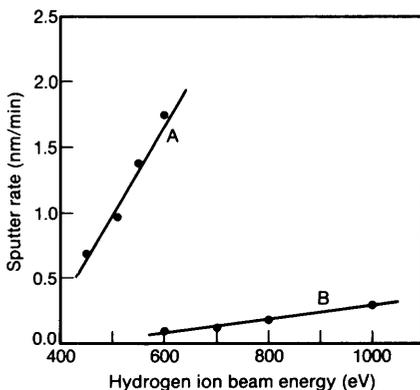


Fig. 1 Amorphous silicon sputter rate vs. hydrogen ion beam energy for the ion beam current density of  $1 \pm 0.05 \text{ mA/cm}^2$  (A) and  $0.3 \pm 0.05 \text{ mA/cm}^2$  (B).

By empirically optimizing the hydrogenation treatment conditions, we have obtained rehydrogenated samples with a photoconductivity and photosensitivity better than those reported in ref. 5. The most photosensitive rehydrogenated a-Si:H we have obtained so far is a sample (#61i) with an air-mass-one (AM1) photo-to-dark conductivity ratio (called "the conductivity ratio" from here on) of  $9.5 \times 10^6$  and an AM1 photoconductivity of  $8.6 \times 10^{-6} \text{ ohm-cm}^{-1}$ . This sample had an optical bandgap of 1.85 eV and a dark-conductivity activation energy of 0.94 eV. We performed two rehydrogenation treatments on this sample, both at  $E = 600 \text{ eV}$  and  $J = 1 \text{ mA/cm}^2$ . In the first treatment, which took 90 min, the sample was not heated, and in the second treatment, which took 30 min, the sample was heated to  $200^\circ\text{C}$ .

#### Posthydrogenation

For posthydrogenation experiments, we used hydrogenation conditions similar to those used for rehydrogenation. The best results were obtained using a-Si deposited by silane glow discharge at  $480^\circ\text{C}$ . The highest quality sample so far had two consecutive hydrogenation treatments. The first treatment was done under the conditions of  $E = 500 \text{ eV}$ ,  $J = 1 \text{ mA/cm}^2$ ,  $T = 250^\circ\text{C}$ , and  $t = 60 \text{ min}$ . In the second hydrogenation treatment,  $E = 600 \text{ eV}$ ,  $J = 0.9 \text{ mA/cm}^2$ ,  $T = 200^\circ\text{C}$ , and  $t = 60 \text{ min}$ . After these posthydrogenation treatments, the sample was annealed at  $300^\circ\text{C}$  in vacuum for two hours. The

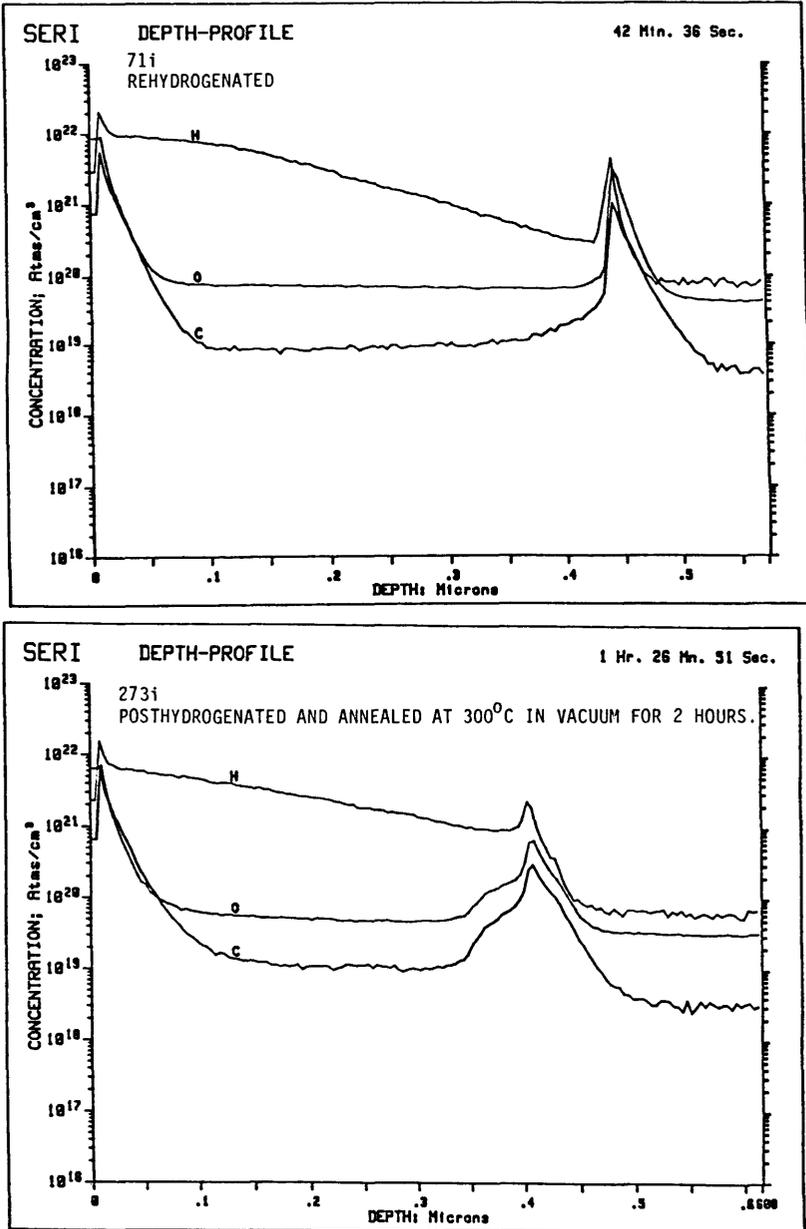


Fig. 2 SIMS depth profiles of a rehydrogenated (top) and a posthydrogenated and annealed a-Si:H (bottom).

resulting a-Si:H had a conductivity ratio of  $1.1 \times 10^5$ , an AML photoconductivity of  $6.3 \times 10^{-6}$  ohm-cm<sup>-1</sup>, an optical bandgap of 1.82 eV, and a dark-conductivity activation energy of 0.86 eV. Generally speaking, the two hour, 300°C annealing after posthydrogenation caused no significant change in the measured optical bandgap, and resulted in improvements (up to a factor of 10) in the conductivity ratio and photoconductivity. Like those of the rehydrogenated samples, the IR absorption spectra of these ion-beam posthydrogenated samples exhibited predominantly SiH bonds.

Secondary ion mass spectroscopy (SIMS) measurements of a rehydrogenated and a posthydrogenated sample (Fig. 2) show that the distribution of hydrogen as a function of distance from the hydrogenated surface (depth profile) is not uniform. The rehydrogenated sample was annealed at only 200°C for one hour after hydrogenation. In addition to this routine 200°C annealing, the posthydrogenated sample was annealed at 300°C for two hours. The first 100 nm of the rehydrogenated sample had a somewhat uniform distribution of hydrogen at the level of  $1 \times 10^{22}$  atoms/cm<sup>3</sup> (20 at.%). Then the hydrogen content decreased exponentially toward the back surface. We think that during the ion-beam hydrogenation the hydrogen ions penetrate a few hundred angstroms into the a-Si and then diffuse toward the front and back surface as atomic hydrogen. The 300°C annealing further enhances the diffusion of hydrogen. Since the measured optical bandgap did not change significantly upon annealing, the hydrogen lost from the front surface during the annealing was very small.

Because of the difficulty of depositing thermal-CVD a-Si in our glow-discharge-deposition system, we studied only three samples, deposited at 500°C, 550°C, and 600 °C, respectively. The conductivity ratios obtained after posthydrogenation were 500 for the 500 °C sample, 130 for the 550°C sample, and 40 for the 600 °C sample. The dependence of the conductivity ratio on the a-Si deposition temperature indicates possible contamination from the glass substrate during thermal-CVD deposition. Further optimizations of the thermal-CVD deposition process and the posthydrogenation and annealing conditions are needed.

Ion-beam posthydrogenations of magnetron-sputtering-deposited a-Si have produced a-Si:H films with properties comparable to those of magnetron-sputtering-deposited a-Si:H that is hydrogenated during deposition [14]. One of the highest quality hydrogenated samples had a conductivity ratio of  $1.0 \times 10^4$ , an AML photoconductivity of  $7.0 \times 10^{-5}$  ohm-cm<sup>-1</sup>, an optical bandgap of 1.86 eV, and a dark-conductivity activation energy of 0.76 eV. This sample was hydrogenated under the conditions of  $E = 600$  eV,  $J = 0.3$  mA/cm<sup>2</sup>,  $T = 250^\circ\text{C}$ , and  $t = 240$  min. The magnetron-sputtering-deposited a-Si samples we studied have high dark conductivity values both before and after hydrogenation. We believe this is due to high impurity levels. SIMS measurements of these samples showed that nitrogen, oxygen, and carbon levels are all above  $10^{20}$  atoms/cm<sup>3</sup>, about two orders of magnitude higher than high-quality glow-discharge-deposited a-Si:H.

### Photostability

For our best quality glow-discharge-deposited a-Si:H samples, the light-induced decay in the photo- and dark conductivities after 20 hours of AML illumination was about a factor of eight, whereas most of our rehydrogenated and posthydrogenated a-Si:H samples showed no detectable Staebler-Wronski effect. The largest light-induced reduction in photoconductivity we have observed so far is the 26% reduction that resulted after we exposed rehydrogenated sample #61i to a 500-mW/cm<sup>2</sup> white light for 19 hours. We also studied the photostability of a posthydrogenated a-SiSn:H alloy sample that contained 0.4 at.% ion-implanted Sn. The AML photocon-

ductivity of this sample after hydrogenation was  $1.4 \times 10^{-5} \text{ ohm-cm}^{-1}$ . After 20 hours of AM1 illumination, this photoconductivity decreased to  $6.1 \times 10^{-6} \text{ ohm-cm}^{-1}$ . This degradation is much greater than that of the ion-beam hydrogenated a-Si:H samples, presumably because of the presence of Sn.

#### CONCLUSIONS

We have studied the rehydrogenation and posthydrogenation of a-Si:H using a Kaufman ion-beam source. When glow-discharge-deposited a-Si or a-Si:H materials are used for hydrogenation, the resulting a-Si:H samples have high photosensitivity and stability. The silicon-hydrogen bonds introduced by the Kaufman ion-beam are predominantly monohydrides. The hydrogen depth profile in ion-beam hydrogenated a-Si:H is not uniform and is possibly the cause of the low photoconductivity values. The posthydrogenations of thermal-CVD and magnetron-sputtering-deposited a-Si are less successful, possibly because of impurity contamination of the starting material.

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