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SYMPOSIUM PROCEEDINGS

**Volume 507**

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# **Amorphous and Microcrystalline Silicon Technology—1998**

Symposium held April 14–17, 1998, San Francisco, California, U.S.A.

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## EFFECT OF PLASMA TREATMENT ON CRYSTALLIZATION BEHAVIOR OF AMORPHOUS SILICON FILMS

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### ABSTRACT

The crystallization of amorphous silicon (a-Si:H) deposited by plasma enhanced chemical vapor deposition (PECVD) by thermal annealing is of great interest for display and silicon-on-insulator (SOI) technologies, though long anneal times (about 20 hrs) at 600 °C are typically required. We report that a room temperature hydrogen plasma exposure in a parallel plate diode type Reactive Ion Etcher (RIE) can reduce this crystallization time by a factor of five. This plasma enhanced crystallization can be spatially controlled by masking with patterned oxide, so that both amorphous and polycrystalline areas can be realized simultaneously at desired locations. This effect is due to the creation of seed nuclei at the surface, which enhance crystallization rates.

### INTRODUCTION

Polycrystalline silicon (polysilicon) is used extensively in the fabrication of thin film transistors (TFTs). Polysilicon formed by the crystallization of amorphous silicon (a-Si) has far superior material and electronic properties than as-deposited polysilicon [1,2]. The most commonly used method to crystallize a-Si is solid-phase crystallization (SPC), which entails annealing in a furnace at a maximum of 600 °C on glass, or at higher temperature and shorter time in a rapid thermal annealer (RTA). Furnace annealing usually requires long anneal times [3]. Various techniques have been tried to reduce the annealing time, e.g. metal induced crystallization [4], germanium induced crystallization [5] and electron cyclotron resonance (ECR) oxygen and helium plasma enhanced crystallization [6]. We have found that a radio frequency (RF) hydrogen plasma exposure at room temperature of plasma-enhanced-chemical-vapor-deposited (PECVD) a-Si:H film can reduce this crystallization time by a factor of five. This method was used for selective crystallization of a-Si, by using SiO<sub>2</sub> as mask during plasma exposure.

In this paper we describe the enhancement process and relate it to the structure of the a-Si:H film.

### EXPERIMENTAL PROCEDURE

Hydrogenated amorphous silicon (a-Si:H) films of varying thickness from 1500 to 4000 Å, were deposited by PECVD using pure silane, on 7059 glass substrates at substrate temperatures of 150 °C, 250 °C and 350 °C, at RF power of ~5 W. The subsequent RF plasma exposure was done in a parallel plate Reactive Ion Etcher (RIE) at room temperature with hydrogen, oxygen or argon, for varying RF power and exposure times. The RF frequency was 13.56 MHz and the RIE electrode area was 250 cm<sup>2</sup>. All samples were annealed in a furnace at 600 °C in N<sub>2</sub> for times ranging from 3 hrs to 20 hrs. UV reflectance measurement [7] was done on all samples to monitor the crystallization process. Based on earlier work [7], the saturation of

growth of the reflectance peak at 276 nm is used as an indication of complete crystallization of the sample. For the selective crystallization experiments, SiO<sub>2</sub> deposited by e-beam evaporation and patterned by lithography and dilute hydrofluoric acid etched, was used as a mask during plasma exposure to realize polysilicon and amorphous silicon on the same substrate.

### EXPERIMENTAL RESULTS

We have studied effect of hydrogen, oxygen and argon plasmas on the crystallization of a-Si:H. Hydrogen plasma has the largest effect, with the crystallization time reduced by a factor of five, and argon plasma had the smallest effect (figure 1). The change in reflectivity at 276 nm is used to monitor the degree of crystallization. The RF power was 200 W, pressure was 50 mtorr and flow rate 50 sccm.

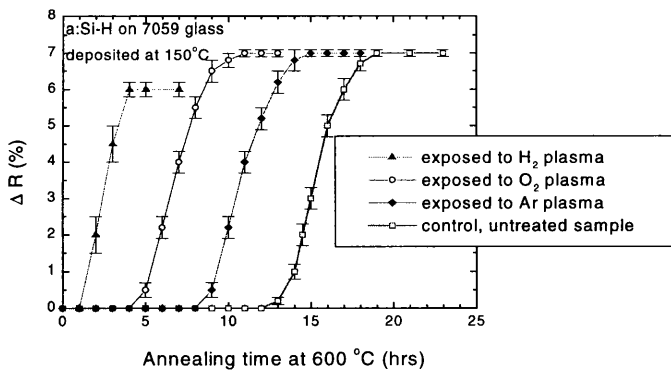


Figure 1. Change in UV reflectance at 276 nm as a function of annealing time for samples exposed to different plasmas.

The crystallization time, defined as the time taken to completely crystallize a-Si:H at 600 °C in N<sub>2</sub> ambient, falls as the RF power of the H<sub>2</sub> or O<sub>2</sub> plasma increases as in figure 2(a). In either case when the RF power is greater than 270 W, the plasma exposure leads to sputter

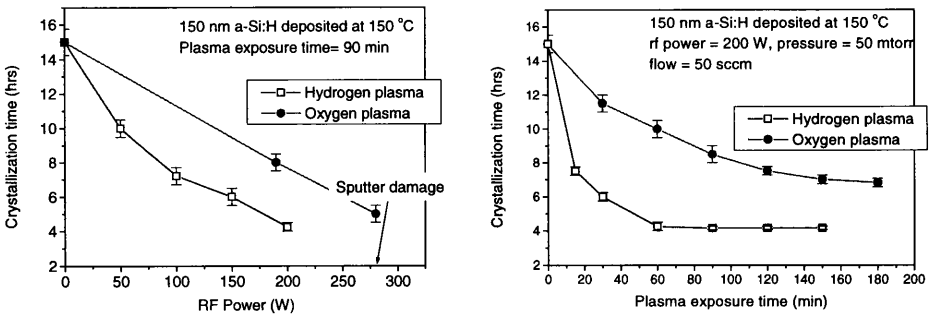


Figure 2. Crystallization time of a-Si:H plasma treated samples as a function of (a) RF power and (b) exposure time. Pressure was 50 mtorr and flow-rate was 50 sccm.

etching of the film which can lead to pits and craters. The crystallization time also reduces as the plasma exposure time increases and saturates after 60 min exposure in case of H<sub>2</sub> and 180 min in case of O<sub>2</sub> plasma exposure respectively, as illustrated in figure 2(b).

The crystallization time also depends on the growth temperature of the a-Si:H films. It falls linearly from ~ 16 hrs to ~ 5 hrs for the untreated control sample as the growth temperature

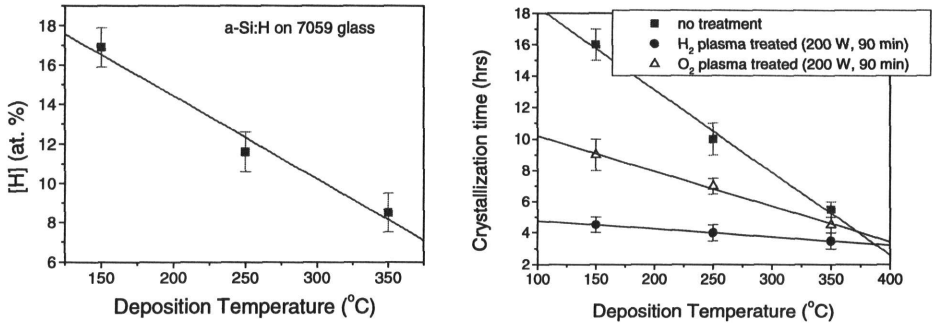


Figure 3. (a) Hydrogen content in the a-Si film as a function of growth temperature, (b) Crystallization time for plasma treated and untreated samples as a function of growth temperature.

increases from 150 °C to 350 °C (figure 3(b)) and this correlates well with the hydrogen content (as measured by IR absorption at 630 cm<sup>-1</sup>) in the film, which also reduces linearly from ~ 16.9 to ~ 8.5 atomic % as the growth temperatures increases from 150 °C to 350 °C (figure 3(a)). Oxygen plasma treated samples also show the same trend. But the hydrogen plasma treated samples show no drastic change in crystallization time with growth temperature (figure 3(b)). From this we infer that, as the PECVD growth temperature is raised, the number of incipient nucleation sites is increased. The relative insensitivity of crystallization time of hydrogen plasma treated sample suggests that, the seeding layer caused by the plasma treatment is the same regardless of starting conditions.

To demonstrate selective crystallization, 100 nm of silicon dioxide (SiO<sub>2</sub>) was deposited by e-beam evaporation. The SiO<sub>2</sub> was then patterned and the samples were exposed to a hydrogen plasma. The SiO<sub>2</sub> was stripped and the samples annealed in furnace. The exposed

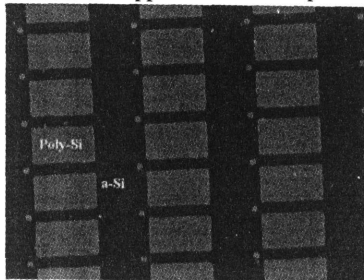


Figure 4. Optical micrograph showing selective crystallization with the light areas (100X230µm<sup>2</sup>) being polycrystalline and the dark areas being amorphous.

areas crystallized completely as expected, with the unexposed areas still amorphous as can be seen in figure 4. This shows that SiO<sub>2</sub> can mask the effect of plasma.

## DISCUSSION

To show that the hydrogen plasma treatment modifies the surface, we dry etched the hydrogen-plasma-treated sample to various depths in SF<sub>6</sub> plasma. We then observed the effect of such etching on the crystallization time. As can be seen in figure 5, a hydrogen plasma treated sample with ~ 40 nm removed, crystallizes at the same time as an untreated sample. This proves that the surface region is responsible for rapid crystallization and the plasma treatment creates seed nuclei in the top ~ 40 nm layer. Figure 6 shows the modified layer thickness for different

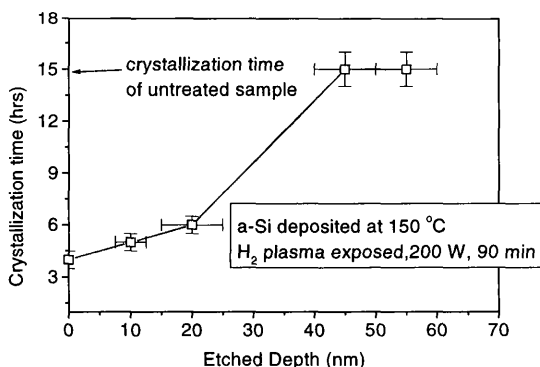


Figure 5. Crystallization time of samples etched to different depths after hydrogen plasma treatment.

exposure times with the RF power held constant at 200 W. The typical modified layer depth is ~ 35 nm. In addition to this effect the hydrogen plasma etches the film at a rate of ~0.2 nm/min at 200 W.

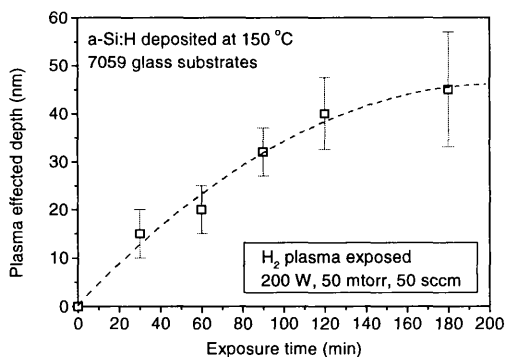


Figure 6. The modified layer thickness as a function of exposure time to hydrogen plasma.

Infrared absorption measurements of the untreated control samples and oxygen plasma treated samples of a-Si:H on silicon substrates, show an absorption peak at  $2000\text{ cm}^{-1}$

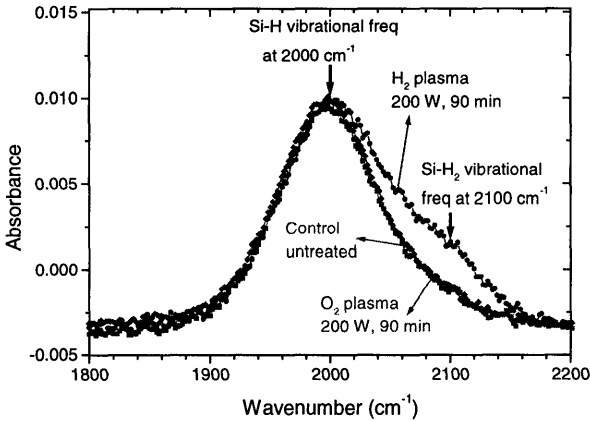


Figure 7. The infrared spectra of a-Si:H deposited at  $250\text{ }^{\circ}\text{C}$  before and after plasma treatment. The hydrogen plasma treated sample shows a shoulder at  $2100\text{ cm}^{-1}$ .

corresponding to Si-H stretching mode [8]. But the hydrogen plasma exposed sample shows a peak also at  $2100\text{ cm}^{-1}$  corresponding to vibrational frequency of Si-H<sub>2</sub> stretching mode [8] as can be seen in figure 7, which shows that hydrogen plasma treatment changes the microstructure of the a-Si:H film leading to increased Si-H<sub>2</sub> bonds.

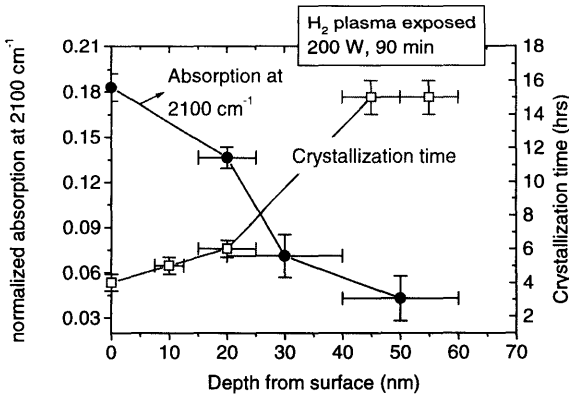


Figure 8. IR absorption at  $2100\text{ cm}^{-1}$  as function of depth from the surface for hydrogen plasma treated sample.

As the samples were progressively etched to different depths, the absorption peak at  $2100\text{ cm}^{-1}$  was reduced. This correlates well with the increase of crystallization time as shown in

figure 8. This is further evidence that the plasma treatment only modifies the properties of the surface layer. The exact microstructure of the surface is not known, however.

## CONCLUSION

We have shown that room temperature exposure to RF hydrogen plasma can dramatically reduce thermal budget for the crystallization of PECVD a-Si:H films. Hydrogen plasma treatment changes the microstructure of the a-Si:H at the surface, creating seed nuclei, which enhances crystallization. We have also shown that this effect can be controlled spatially resulting in polycrystalline silicon and amorphous silicon areas on the same substrate.

## ACKNOWLEDGEMENTS

This work was supported by DARPA through ONR [N66001-97-1-8904] and by DOE through the Princeton Program in Plasma Science and Technology. Rainer Platz's help in calculating the hydrogen content of the a-Si:H films is appreciated.

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