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SIMS Study of Elemental Diffusion During Solid Phase Crystallization of Amorphous Silicon

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SIMS Study of Elemental Diffusion During Solid Phase Crystallization of Amorphous Silicon

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ABSTRACT

Crystallization of hydrogenated amorphous silicon (a-Si:H) films deposited on low-cost substrates shows potential for solar cell applications. Secondary ion mass spectrometry (SIMS) was used to study impurity incorporation, hydrogen evolution, and dopant diffusion during the crystallization process.

1. Objectives

Thin-film silicon solar cells are produced on a variety of low-cost substrates by a variety of methods. Polycrystalline silicon has better electronic transport properties than hydrogenated amorphous silicon (a-Si:H)[1], and solar cells produced from these films are not subject to light-induced degradation effects. Solar cell modules with adequate efficiency (8-9%) have been produced from crystallized hydrogenated amorphous silicon (a-Si:H) films grown by plasma-enhanced chemical vapor deposition (PECVD).[2] However, deposition of electronic-grade a-Si thin films by PECVD is typically done at a low rate, between 1 – 10 Å/s. Higher deposition rates (greater that 100 Å/s) of good quality a-Si:H films can be achieved by hot wire chemical vapor deposition (HWCVD).[3]

Low cost substrate materials e.g. glass and stainless steel, have constituents that can be detrimental to material quality if incorporated into the crystallized silicon, and dopant diffusion can diminish device quality. For these experiments, SIMS depth profile analysis after film crystallization is used to study hydrogen and dopant diffusion, substrate impurity incorporation and the effectiveness of barrier coatings.

2. Technical Approach

Films of a-Si:H were deposited by HWCVD and PECVD onto low-cost substrates. Solid phase crystallization (SPC) was achieved by annealing the films using a hot plate in an N_2 ambient and also by using a tube furnace. Determination of crystallinity is achieved in real-time by reflectance measurements[4] in the hot plate setup and verified by XRD.

SIMS was used to study the incorporation of impurities from the various substrate at different anneal times and temperatures. SIMS measurements were taken by a Cameca IMS-5F at 14.5keV Cs^+ for detection of light elements and dopants, and 8.0keV $O2^+$ for detection of metals.

3. Results and Accomplishments

3.1 Crystallized Silicon on Stainless Steel Substrates

Initial experiments were conducted on a-Si:H films deposited directly on thin stainless steel substrates. Figure 1 shows that the crystallized a-Si:H films have large quantities of metallic impurities introduced during the anneal. A thin layer of SiN_x deposited prior to the a-Si:H was discovered to provide an effective impurity diffusion barrier. However, the roughness of the steel substrate degrades the depth resolution in the SIMS depth profiles and complicates the understanding of diffusion measurements. Non-uniform lateral distribution of impurities and optical microscopy, indicated cracks in the film, most likely due to a large mismatch in the coefficient of thermal expansion (CTE) between silicon and steel. Poor depth resolution and film cracking during SPC shifted our focus to glass substrates.

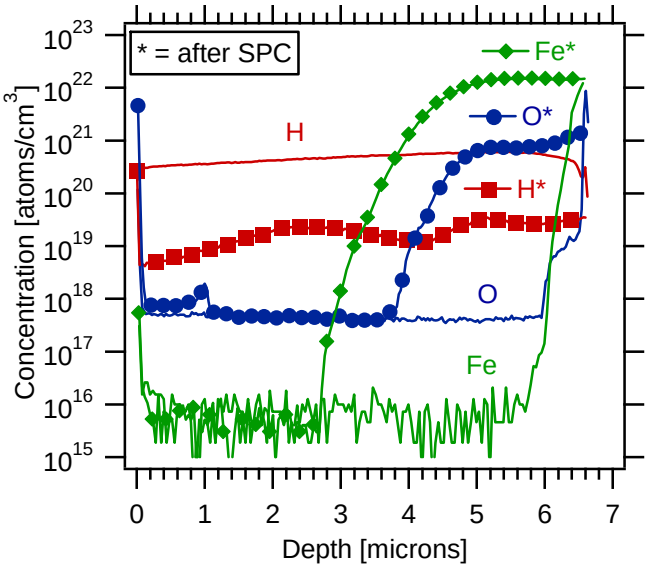

Fig. 1. SIMS impurity concentrations of the indicated elements in a 7-micron Si film on stainless steel that was crystallized from a-Si:H at 550°C for 91 hours.

3.2 Crystallized Silicon on Glass Substrates

Samples for SPC were grown directly on Corning 1737F glass. After film crystallization, no detectable impurities were introduced from the glass, even at temperatures up to 575°C. The oxygen content did not change during SPC, remaining at about 10^{18} /cm^3, lower than what is normally found in CZ-silicon.

Comparisons of different anneal temperatures were made on samples of a-Si:H deposited on SnO_2-coated Corning-1737F glass, before and after SPC. SnO_2 is

commonly used as a transparent conducting oxide in a-Si:H solar cells. Textured SnO_2 aids in light trapping, but creates difficulties in for SIMS depth profiling; and even "smooth" SnO_2 contains some roughness. A thin layer of P-doped silicon (n-layer) was deposited prior to the intrinsic (i) layer. SIMS depth profiles showed approximately 100nm diffusion of P and O during SPC.

3.3 Hydrogen in Crystallized Silicon

Hydrogen is known to evolve from a-Si during high temperature anneals before crystallization and it is important to know at what point during nucleation and crystallization the H evolves. Experiments were performed to study the evolution of hydrogen in the SPC of a-Si:H process. Samples from multiple points in the crystallization process (indication from optical reflectance measurements) were measured. Figure 2 shows increasing H evolution with anneal T in samples that were annealed for 4 hours.

Comparisons were also made on samples of a-Si:H films containing 14 at.% (high) H and 4 at.% (low) hydrogen. The high hydrogen films were grown at a lower substrate temperature and have higher O contents. Even after crystallization, higher H levels were observed in the "high H" films than in the "low H" films. This suggests a higher defect density that traps hydrogen.

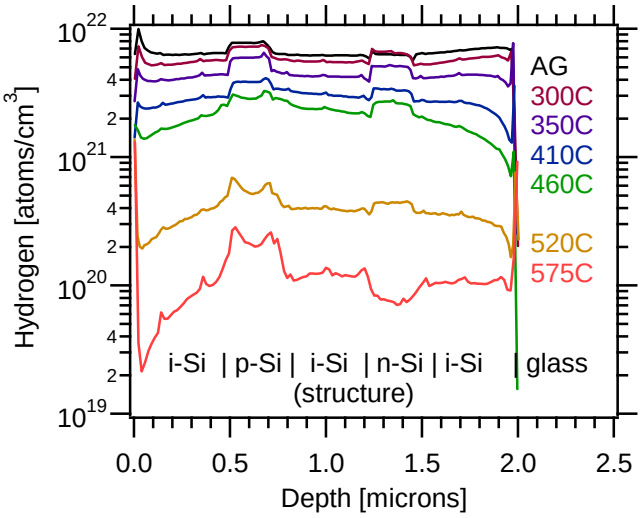

Fig. 2. a-Si:H (i-p-i-n-i) structure showing increased hydrogen evolution at higher anneal temperature.

3.4 Dopant Diffusion During the SPC Process

SIMS was also used to study B and P dopant diffusion during the anneal process. Structures were grown comprising both n-type and p-type a-Si:H layers sandwiched between intrinsic layers (i-p-i-n-i/glass). Samples were annealed at different temperatures for 4 hours and then depth-profiled by SIMS. We found that B (at ~$2x10^{19}$ cm^{-3}) did not move significantly during SPC. However, P (at ~ 10^{21} cm^{-3}) did diffuse considerably, as shown in Fig. 3. High mass resolution measurements of ^{31}P in a-Si:H are also challenging due the high levels (1-10 at.%) of H, which can form $^{31}Si^{1}H$ secondary ions.

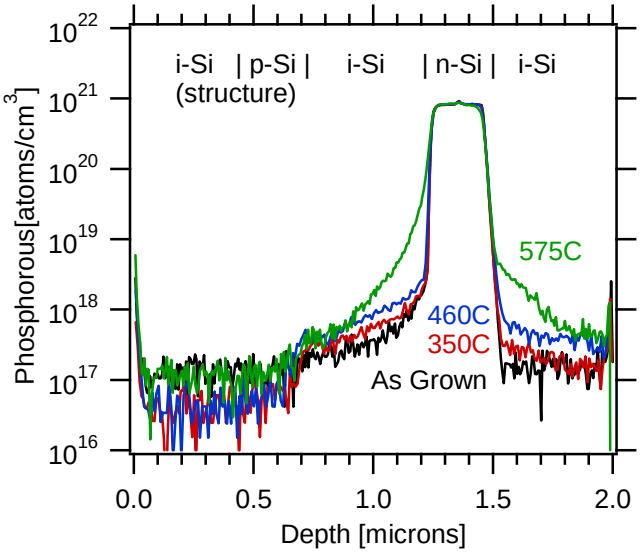

Fig. 3. SIMS P concentrations vs anneal temperature.

4. Conclusions

Problems with cracking occur with stainless steel as a substrate for a-Si:H crystallization, although SiN_X performs well as a diffusion barrier. SPC of films on 1737F glass showed no evidence of impurities from the glass, even up to annealing temperatures of 575°C. P dopant diffusion occurs during SPC, and hydrogen release occurs prior to nucleation and crystal growth. Crystallization of these films shows potential for solar cell applications.

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