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Structural properties of a-Si films and their effect on aluminum induced crystallization

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In this paper, we report the influence of the structural properties of amorphous silicon (a-Si) on its subsequent crystallization behavior via the aluminum induced crystallization (AIC) method. Two distinct a-Si deposition techniques, electron beam evaporation and plasma enhanced chemical vapor deposition (PECVD), are compared for their effect on the overall AIC kinetics as well as the properties of the final poly-crystalline (poly-Si) silicon film. Raman and FTIR spectroscopy results indicate that the PECVD grown a-Si films has higher intermediate-range order, which is enhanced for increased hydrogen dilution during deposition. With increasing intermediate-range order of the a-Si, the rate of AIC is diminished, leading larger poly-Si grain size.

The use of poly-crystalline silicon (poly-Si) thin films as absorber layers for solar cells have received considerable interest due to their potential for combining the advantages of crystalline silicon (abundance, non-toxicity, high efficiency) with those of the thin film approach (reduced active material usage, low cost/lightweight substrates). Methods that involve the crystallization of a previously deposited amorphous silicon (a-Si) film proved to be among the most effective for obtaining poly-Si films on foreign substrates.1,2 One such technique is aluminum induced crystallization (AIC), which utilizes a sacrificial aluminum layer that enables crystallization of a-Si at low temperatures (as low as 150°C has been reported3). AIC is realized by annealing an a-Si/Al film stack at temperatures below the Al-Si eutectic temperature, 577°C.4 The crystallization takes place by the consecutive dissolution and re-precipitation of Si in Al at the a-Si/Al interface, where the driving force is the difference in the respective solubilities of a-Si and crystalline Si in Al.5 From this point of view, it is clear that the a-Si film properties, in particular its bonding, would have a significant influence on the dissolution/re-precipitation behavior of Si in Al, thus affect the AIC process.

For this study, two amorphous Si (a-Si) deposition techniques, e-beam evaporation and PECVD, are compared as means for producing the initial a-Si film for AIC. Both of these techniques have important advantages from an application standpoint: e-beam evaporation enables high deposition rates and a precise doping profile, whereas PECVD is more compatible with large area applications. In addition, while many parameters affecting the AIC process such as annealing temperature,6 Al grain structure7,8 and thickness and structure of the AlOx layer at the Si/Al interface9,10 have been previously studied; the influence of the a-Si layer on AIC layer has largely been unexplored (barring a study focusing on the hydrogen content of sputtered a-Si films11).

The AIC experiments were carried out using a a-Si/Al/SiNx/glass stack configuration, wherein the SiNx layer serves as a buffer to prevent any contamination from the glass substrate. Schott AF32 was used as glass substrate, SiNx buffer layer (approximately 80nm) was deposited by PECVD, and an Al layer of 180nm was grown using thermal evaporation. In order to isolate the a-Si layer as the sole variable, all samples section were produced from the same Al/SiNx/glass batch. Following
Table I. a-Si deposition method and parameters for various sample sets.

| Batch Name | a-Si Deposition | Substrate Temperature (°C) | SiH₄:H₂ Ratio |
|------------|----------------|-----------------------------|---------------|
| E-RT       | E-beam         | 25                          | N/A           |
| E-HT       | E-beam         | 420                         | N/A           |
| P-9        | PECVD          | 25                          | 1:9           |
| P-29       | PECVD          | 25                          | 1:29          |

A 4-day exposure in clean room to induce AlOₓ formation, samples were separated into 4 batches and a-Si depositions were carried out. The 4 different a-Si deposition runs and their corresponding sample designations are given in Table I.

All of the a-Si layers were targeted for 360nm. For the e-beam deposition runs (E-RT and E-HT) the base pressure of the e-beam system was 1-2 x 10⁻⁷ Torr, which rose up as high as 8 x 10⁻⁷ Torr during evaporation. The deposition rate was 1.5 nm/sec. The PECVD depositions (P-9 and P-29) were done using a capacitively coupled plasma system with a base pressure of 5 x 10⁻⁶ Torr and an operating pressure of 1 Torr. A mixture of 10%SiH₄-90%H₂ was used as the silane source. For batch P-9, the silane mixture was flown into the chamber at 350 sccm, resulting in a deposition rate of approximately 0.4 nm/sec. For batch P-29, the silane mixture was flown at 100 sccm and further diluted by H₂ at 200 sccm, corresponding to a deposition rate of about 0.15 nm/sec. During deposition cycles, additional quartz and Si-wafer pieces were inserted into the chamber to enable Raman and FTIR analysis, respectively, of the grown a-Si films. The a-Si/Al/SiNₓ/glass stacks were then annealed in classical tube furnace (when possible, together) for varying times between 420 and 450°C. The AIC process was monitored predominantly by optical micrographs obtained by reflecting the light through the glass substrate side of the samples.

In-situ AIC during e-beam Si deposition

As seen in Table I, the e-beam deposition was done by two different substrate temperatures, room temperature (E-RT) and 420°C (E-HT). The optical micrographs taken from E-RT and E-HT samples upon deposition (without any furnace anneal) are given in Fig. 1(a) and 1(b), respectively. While there is no indication of crystallization at the a-Si/Al interface for the E-RT sample (Fig. 1(a)), small dendritic Si crystallites are easily observable for the E-HT sample (Fig. 1(b)), suggesting that the nucleation has already begun by the end of a-Si deposition in the latter case.

Furnace annealing experiments

Selected micrographs showing the a-Si/Al interface of samples from batches E-RT, E-HT, P-9 and P-29 at varying annealing times are given for 420 and 450°C annealing in Figs. 2 and 3, respectively. For both annealing temperatures, samples from batches with e-beam deposited a-Si (Figs. 2(a) and 2(b), Fig. 3(a) and 3(b)) yielded a considerably higher crystallization rate, compared to samples from batches with PECVD deposited a-Si (Figs. 2(c) and 2(d), Fig. 3(c) and 3(d)).

![Optical micrographs from the a-Si/Al interface taken from samples from batches a) E-RT, and b) E-HT. The interface for the E-RT sample appears featureless, while small crystal nuclei are visible for the E-HT sample.](image-url)
When the crystallization behavior of the E-RT and E-HT samples are compared, it is seen that the latter has higher crystallization rate and smaller crystallite size. This was an expected outcome, as the nucleation had readily started for E-HT prior to any annealing (as seen in Fig. 1), thus the nucleation barrier that had to be overcome for E-RT was not present. This can clearly be observed by comparing the micrographs from the early stages (15 min for 420°C and 10 min for 450°C) for both samples; for E-RT nucleation has not yet started, while E-HT is well in its growth stage.

In the micrographs given for the P-9 sample set (Figs. 2(c) and 3(c)), voids of diameters on the order of 50-100 µm is visible, whereas no such voids are seen for P-29 (Figs. 2(d) and 3(d)). Excessive residual hydrogen in PECVD grown a-Si is known to cause micro-voids upon subsequent heat treatments.\textsuperscript{12,13} The hydrogen content in the respective films are discussed below. The AIC kinetics also differed between the two sample sets; the necessary annealing time for initial nucleation as well as the completion of crystallization for P-9 was significantly shorter than that for P-29.

**Final poly-Si grain structure**

After the completion of crystallization, the top Al-Si layer was removed via mechanical polishing and the grain structure of each sample was investigated by electron backscatter diffraction (EBSD). The EBSD images taken from samples annealed at 450°C are given in Fig. 4. As expected,
FIG. 4. EBSD images taken from fully crystallized samples annealed at 450°C, a) E-RT, b) E-HT, c) P-9, and d) P-29. The colors represent the orientation of grains according to the color code given in the lower left corner inset.

an inverse relation between grain size and crystallization rate was observed, where the P-29 sample has the highest grain size and E-HT sample has the lowest. No significant difference in grain orientation is apparent, with all samples showing a preference toward (100), as indicated by the dominance of red/orange color grains.

**Characterization of a-Si films**

In order to elucidate on the observed differences in crystallization kinetics between the four sample sets, a-Si films from each batch was characterized using Raman spectroscopy and FTIR. In Fig. 5, the Raman spectra for a-Si samples deposited on quartz substrates during each deposition run is given. For all samples, the characteristic peaks associated with transverse acoustic (TA), longitudinal acoustic (LA), and transverse optic (TO) modes are readily visible in the vicinity of 150, 300 and 480 cm$^{-1}$, respectively (for simplicity, only the peak positions of TA and TO modes are indicated on the graph). In addition, PECVD-grown samples (P-9 and P-29) show a small feature near 620 cm$^{-1}$, which has previously been attributed to Si-H wagging modes in literature. Two of these features, the TA and TO peaks, are considered to be crucial for the bond structure of a-Si. Accordingly, the line width of the TO peak is directly proportional to the short range disorder, while a greater intensity ratio between TA and TO peaks ($I_{TA}/I_{TO}$) is known to indicate a higher intermediate range disorder. Based on this consideration, it appears that E-RT sample has higher short range disorder compared to the rest of the samples and no significant difference for TO line width is apparent between E-HT, P-9 and P-29. The $I_{TA}/I_{TO}$ ratio for each spectrum, however, shows a more distinct trend. The intermediate range disorder for the a-Si films, based on the $I_{TA}/I_{TO}$ ratios, ranks as follows (from the most disordered
FIG. 5. Normalized Raman spectra taken from the as-deposited a-Si films from batches E-RT, E-HT, P-9 and P-29. Spectra are stacked on the same graph (with varying intensity offsets) for ease of comparison. Approximate positions of the transverse acoustic (TA) and transverse optical (TO) peaks are indicated on the graph.

FIG. 5. Normalized Raman spectra taken from the as-deposited a-Si films from batches E-RT, E-HT, P-9 and P-29. Spectra are stacked on the same graph (with varying intensity offsets) for ease of comparison. Approximate positions of the transverse acoustic (TA) and transverse optical (TO) peaks are indicated on the graph.

to the least): E-RT > E-HT > P-9 > P-29. Here, the higher order observed for both of the PECVD samples (P-9 and P-29) can be explained by the presence of hydrogen in the a-Si films. Morell et. al. discusses the strain relieving effect of hydrogen on the a-Si network as it pertains to their comparison between PECVD and (un-hydrogenated) sputtered films.16

As discussed earlier, the dissolution of a-Si in Al and its subsequent precipitation is at the core of the AIC process. The solubility of a-Si is correlated with its chemical potential, $\mu_{a\text{-Si}}$, where the higher the $\mu_{a\text{-Si}}$ (i.e., lower the stability of the a-Si film) the easier the dissolution process will occur. From this standpoint, keeping all other process variables constant, it could be expected that higher disorder in the a-Si film would correspond to lower activation energies for its dissolution in Al, resulting in higher crystallization rates. The trend given above for the disorder in different types of a-Si films based on Raman spectra is in accord with the crystallization rates observed by optical microscopy with one exception: the disorder in the E-HT sample is greater than the E-RT sample, though the latter has higher crystallization rate. This has already been explained by the in-situ nucleation process that had occurred during the a-Si deposition of the E-HT sample.

To further investigate the nature of hydrogen bonding in the PECVD samples, FTIR spectroscopy was carried out on P-9 and P-29 a-Si layers grown on Si-wafer substrates, as shown in Fig. 6. In Fig. 6(a), the wavenumber range that is relevant to the bending modes of Si-H bonds are shown. In both samples a peak around 640 cm$^{-1}$ is observed, which is associated with the bend-rock-wag modes, while in P-9 two additional peaks between 800 and 900 cm$^{-1}$ is seen. These two peaks correspond to bend/scissors and wag modes, and are indicative of the presence of SiH$_2$.13 Further evidence of this observation is found in Fig. 6(b) through 6(d), where the spectra showing the stretching modes from each sample is given. Two peaks are identified in this range: the low stretching mode near 2000 cm$^{-1}$, related to SiH bonds; and high stretching mode around 2070-2090 cm$^{-1}$, which is associated with SiH$_2$ bonds.11 It is clear from comparing Figs. 6(c) and 6(d) that sample P-9 has significantly higher SiH$_2$ bonds compared to P-29, which are known to result in poor quality a-Si films.13 This observation is explained by the fact that at high H$_2$ dilution (in this case P-29), the additional hydrogen in the system “attacks” the weakly bound SiH$_2$, dissociating it to the more stable form of SiH. While
FIG. 6. Normalized FTIR spectra taken from the as-deposited a-Si films from batches P-9 and P-29: a) Bend modes, b) stretch modes, c) Gaussian deconvolution of P-9 stretch mode, and d) Gaussian deconvolution of P-29 stretch mode.

the total hydrogen quantity in P-9 and P-29 films do not differ significantly, the hydrogen in P-29 is predominantly in SiH form, leading to higher film stability (thus lower AIC rates). In addition, the weakly bound SiH2 in the P-9 sample lead to hydrogen micro-voids upon annealing.

In conclusion, a strong, inverse correlation between intermediate range disorder of a-Si and the rate of crystallization was observed. The presence of hydrogen improves the intermediate range order in the deposited a-Si film, resulting in a lower crystallization rate and larger final poly-Si grain size. Increased H2 dilution during PECVD deposition promotes SiH instead of SiH2, preventing microvoid formation during subsequent annealing cycles.

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1. C. Becker, D. Amkreutz, T. Sontheimer, V. Preidel, D. Lockau, J. Haschke, L. Joughies, C. Klimm, J.J. Merkel, P. Plocica, S. Steffens, and B. Rech, Sol. Energy Mat. Sol. Cells 119, 112 (2013).
2. D. Van Gestel, I. Gordon, and J. Poortmans, Sol. Energy Mat. Sol. Cells 119, 261 (2013).
3. Y. J. Yang, Z. M. Wang, and E. J. Mittemeijer, J. Appl. Phys. 102, 113523 (2007).
4. O. Nast, S. Brehme, S. Pritchard, A. G. Aberle, and S. R. Wenham, Sol. Energy Mat. Sol. Cells 65, 386 (2001).
5. J. Schneider, A. Schneider, A. Sarikov, J. Klein, M. Muske, S. Gall, and W. Fuhs, J. Non-Cryst. Solids 352, 972 (2006).
6. S. Gall, M. Muske, I. Sieber, O. Nast, and W. Fuhs, J. Non-Cryst. Solids 299–302, 741 (2002).
7. O. Nast and A. J. Hartman, J. Appl. Phys. 88, 716 (2000).
8. E. Stinziani, K. Dunn, Z. Zhao, M. Rane-Fondecaro, H. Efstatiadis, and P. Halder, in 34th IEEE Photovoltaic Specialists Conference, Philadelphia, USA (2009), p. 001643.
9. H. Schneider, J. Klein, M. Muske, S. Gall, and W. Fuhs, J. Non-Cryst. Solids 338–340, 127 (2004).
10. M. Stöger-Pollach, T. Walter, M. Muske, S. Gall, and P. Schattschneider, Thin Solid Films 515, 3740 (2007).
11. X. Zhai, R. Tan, W. Wang, J. Huang, F. Zhuang, S. Dai, and W. Song, J. Cryst. Growth 402, 99 (2014).
12. S. Muramatsu, R. Suzuki, L. Wei, and S. Tanigawa, Sol. Energy Mat. Sol. Cells 34, 525 (1994).
13. A. V. Shah, Thin-Film Silicon Solar Cells (EPFL Press, Lausanne, Switzerland, 2010).
14. G. Morell, R. S. Katiyar, S. Z. Weisz, and I. Balberg, J. Non-Cryst. Solids 194, 78 (1996).
15. P. Danesh, B. Pantechev, E. Liaokapis, and B. Schmidt, Journal of Mater. Sci.: Materials in Electronics 14, 753 (2003).
16. G. Morell, R. S. Katiyar, S. Z. Weisz, H. Jia, J. Shinar, and I. Balberg, J. Appl. Phys. 78, 5120 (1995).