Optically Assisted Metal-Induced Crystallization of Thin Si Films for Low-Cost Solar Cells

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ABSTRACT

Optically assisted, metal induced crystallization (MIC) was used to convert amorphous Si films, deposited on Al coated glass substrates, into polycrystalline Si (pc-Si). The study investigated the effects of deposition temperature, process temperature, and film thickness on the grain orientation, grain size, and crystallization front of the processed films. Furthermore, we have attempted to examine the role of Al in MIC — in particular, whether the metal can be confined to the interface while grain enhancement occurs.

INTRODUCTION

A thin-film Si solar cell consists of a low-cost substrate, such as glass, that supports a very thin (~10 µm) Si solar cell. Because thin Si can absorb only a fraction of the useable solar spectrum, the absorption must be enhanced by suitable light-trapping structures. Recent calculations show that by including practical light-trapping designs, only about 10 µm of Si is needed to yield absorption comparable to that of thick wafers [1]. Such a film must also meet other requirements pertaining to the grain size and the grain boundary structure to make the device amenable to low carrier-recombination and concomitant high device efficiency.

We have developed a thin Si cell design that incorporates a number of high-efficiency features and can be fabricated by low-cost processing [2]. The cell design is illustrated in Figure 1, where a glass substrate is coated with Al/Cr, followed by a layer of a-Si or fine-grain pc-Si. The rest of the structure is generic. One of the important fabrication issues in this structure is how to make a suitable crystalline Si film at temperatures compatible with the glass substrate. The layer of Al has multiple roles — to serve as a back reflector, provide a stress-relief interface so that the thick Si film does not peel off, and provide an intrinsic layer for impurity gettering.

Because the cell configuration involves a low-cost glass substrate, the device processing must be performed below 550°C, which is the softening temperature of a typical soda-lime glass. There are several ways to obtain a thin pc-Si layer. One way is to start with an amorphous Si film and convert it into pc-Si by thermal annealing. However, thermal annealing requires long times, temperatures higher than 550°C, or both. Another disadvantage of this approach is that the grain size is typically less than 0.1 µm [3]. A more tempting approach for
fabricating the proposed device is to use Al for converting a-Si into crystalline Si by MIC. This approach has been used quite successfully in display device technology [4]. However, MIC of a-Si based on thermal annealing alone is known to produce films that are saturated with the metal. In addition, such a process requires long annealing times (>10 minutes), high temperatures, or both. We have attempted to use optical excitation to promote crystallization and grain growth in thin films. This paper describes some of our experimental results on MIC—primarily on the grain growth, orientation, and Al contamination of the Si film.

EXPERIMENTAL DETAILS

We have performed experiments to investigate method(s) suitable for fabricating the cell structure shown in Figure 1. A prerequisite for low-cost fabrication is that the crystallization process should be rapid and be performed at a low temperature, typically less than 550°C. The a-Si films were deposited on the metal-coated quartz substrates by a number of different methods. These methods include sputtering, plasma CVD, and hot-wire CVD processes. In some cases, the deposition temperature was changed to study its effect on crystallization; the deposition temperature ranged from room temperature to 500°C. Typical deposition rate was quite high – ranging from 0.005 to 0.05 µm a minute, depending on the deposition technique. The film thickness ranged between 1 to 10 µm. During deposition of a thick film, the film could experience considerable annealing. The samples were then processed to study MIC.

Because thermal annealing is typically a slow process, we explored optical excitation to enhance the crystallization and grain growth. Our initial work compared thermal processing and optical processing to achieve MIC of a thin layer of a-Si. These studies clearly showed that optical excitation can enhance crystallization. These conclusions are also apparent in the results described in this paper. Optical processing is done in a quartz furnace, shown schematically in Figure 2a. It consists of a quartz muffle, illuminated by a bank of tungsten-halogen lamps through a diffuser plate to improve the uniformity of light within a 6-in x 4-in process zone. The furnace has a provision to control the intensity of light that illuminates the sample. A computer control allows a pre-selected, light-intensity vs. time profile to illuminate the sample. Because in this process the temperature is determined by the optical flux absorbed by the sample, the temperature profile acquired by a sample (for a given incident intensity profile) depends on the structural configuration of the sample. A typical temperature profile during processing is shown in Figure 2b. It is important to note that the profile, optimized for obtaining large-grain films, has much longer rise and fall times compared with a regular RTP process. The primary process parameters that were varied are the maximum light intensity (that determines the maximum temperature) and the dwell-time at the maximum temperature.

As-deposited Si films were characterized to determine any crystallization (or MIC) resulting from thermal annealing during the deposition process. SEM and optical microscopic examinations of the films grown at different temperatures indicated: 1) a-Si films adhere well only on the regions of metal coating. This is true at all deposition temperatures. 2) The a-Si/Al samples that were thermally processed for a short time (<20 min) at temperatures lower than 400 °C, show little evidence of crystallization. 3) Surface morphology of the a-Si/Al films deposited at less than 500°C is fairly smooth. At higher deposition temperatures, a blistering or bubbling
The deposited a-Si/glass films were processed in an optical furnace using Ar as the process gas. The process conditions were varied to yield maximum temperatures between 200\(^\circ\)C and 600 \(^\circ\)C and processing times between 1 and 4 min. Process time and temperatures are much less than those for thermal MIC. After optical processing, the films were characterized to investigate start of crystallization, propagation of the crystallization front, grain size, and Al/Si distribution profile resulting from different process conditions.

Optical processing can initiate nucleation and then lead to a grain-enhancement process. The nucleation initiates from the Al-Si interface at temperatures as low as 200\(^\circ\)C and within a very short time (a few minutes). Figures 3a and 3b show XRD Spectra of a film deposited at <100\(^\circ\)C and then processed for 3 min at a maximum temperature of 200\(^\circ\)C, respectively. An initiation of crystallization can be clearly seen, with a preferred orientation of (220). One can also see a large Al peak indicative of the unused Al. The initial Al thickness was 2 \(\mu\)m.

The TEM results show that the initial part of the optical process leads to a nucleation occurring over the entire interface. Then a crystallization front propagates away from the interface converting a-Si into crystalline Si. These features can be seen in Figure 4, which is TEM a cross section of a partially crystallized Si film on a glass substrate. The film, 6 \(\mu\)m thick, was deposited at 250\(^\circ\)C and processed for 3 min at 460\(^\circ\)C. The various regions of the structure, are identified in the figure. The largest grain size near the Al interface is about 0.1 \(\mu\)m and decreases toward a-Si. From this figure, it is clear that 3 min of optical processing time was not sufficient to crystallize the entire film at 460\(^\circ\)C.

Other experimental evidence shows that an increase in the process time and/or temperature leads to enhancement of grain size while the crystallization spreads over the entire thickness of the a-Si
film, with two preferred orientations. However, there appears to be an “incubation temperature” at which the grain enhancement begins. We have carried out studies to investigate crystallization at different temperatures. The samples were optically processed to change the maximum light intensity while keeping the process time constant. Figure 5 shows the results in terms of XRD intensity for the two orientations. From these plots, one may also infer that thinner films can be crystallized more rapidly than thicker ones.

One of the objectives of our study is to decipher the role of Al in crystallization of a-Si. We have performed analyses to investigate mixing of Si and Al. The results of micro-EDX analysis done at different points over the cross section of a processed sample are shown in Figure 6. It is seen that the film composition changes drastically from Al-dominated to Si-dominated in less than 1 µm from the Al/Si interface, whereas the crystallization has spread more than 3 µm into a-Si. This finding implies that it is possible to limit Al within a thin layer in the vicinity of the Al/Si interface and keep the crystallization going deep into Si layer. Thus, a high Al concentration may not be necessary for spreading crystallization.
DISCUSSION AND CONCLUSIONS

We have investigated the possibility of applying optically assisted MIC in making large-area mc-Si thin-film solar cells. We found that during optical processing, crystallization of a-Si can start at about 200ºC in less than 3 minutes. This crystallization becomes much stronger at temperatures close to 450ºC. By controlling the process conditions, it is possible to confine Al in the vicinity of the Si-Al interface leaving the crystallized film (away from the interface) with a low Al concentration.

**Figure 5.** Intensity of Si (111) and Si (220) peaks in the XRD spectra of processed samples as functions of processing temperature. A “jump” of peak intensity around 490ºC can be observed for 10-µm-thick sample.

**Figure 6.** (Left) The TEM image showing the positions where the EDX analysis was performed over the cross section of a processed sample. (Upper) EDX spectra correspond to points 1, 2, and 3, respectively.
It is fruitful to assess if the major mechanisms proposed for thermal MIC apply to optical processing. We can comment on the following two mechanisms:

- Crystallization is induced by diffusion of Al into Si. The diffusion changes the Si-Si bonding from covalent to metallic and contributes to a large reduction in the activation energy, concomitantly making the bonding states in a-Si to become like those in crystalline Si phase. Because, this process can occur only in the regions that have high metal concentration.
- Crystallization is mediated by Al silicide, which is formed at 150° to 250°C and dissociates at 350°C. However, this theory cannot explain why crystallization becomes much stronger in thick samples when the temperature is higher than 500°C (see Figure 5), at which Al silicide can hardly exist.

Based on our observations, we propose explanation of the optically assisted, Al-induced crystallization and grain enhancement of thick samples as follows:

- Optical processing may be generating a non-uniform temperature distribution within the film structure, especially at the Al-Si interface where energy can be locally absorbed producing a higher temperature spike.
- In high-temperature (>450°C) optical processing, although the monitored temperature is lower than the eutectic point of Al-Si system, melting in the local regions around the Al/Si interface may still occur. This local melting will induce crystallization at the interface area, and this crystallization can be much stronger than the crystallization caused by Al-Si intermixing at a solid phase.
- For thick samples, once the initial crystallization has occurred, it is possible to continue crystallization and grain enhancement via injection of defects. We believe that in this process vacancies are injected into Si, especially when temperature is below 450°C, which can promote grain growth. This could suggest that following a high temperature dwell, the optical power be reduced to stimulate grain enhancement.

One may think that a preferred approach of crystallization would be to deposit the a-Si film at a higher temperature and then use optical processing. However, results to date seem to indicate that the effect of optical processing is somewhat diminished if the film is deposited at higher temperatures. Thus, contrary to our intuition, low-temperature deposition appears to favor crystallization during optical processing.

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REFERENCES