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Description	

# **Precursor Cat-CVD a-Si films for the formation of high-quality poly-Si films on glass substrates by flash lamp annealing**

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## **Abstract**

Amorphous Si (a-Si) films with lower hydrogen contents show better adhesion to glass during flash lamp annealing (FLA). The 2.0- $\mu\text{m}$ -thick a-Si films deposited by plasma-enhanced chemical vapor deposition (PECVD), containing 10% hydrogen, start to peel off even at a lamp irradiance lower than that required for crystallization, whereas a-Si films deposited by catalytic CVD (Cat-CVD) partially adhere even after crystallization. Dehydrogenated Cat-CVD a-Si films show much better adhesion to glass, and are converted to polycrystalline Si (poly-Si) without serious peeling, but are accompanied by the generation of crack-like structures. These facts demonstrate the superiority of as-deposited Cat-CVD a-Si films as a precursor material for micrometer-thick poly-Si formed by FLA.

## **Keywords**

Catalytic CVD, Flash lamp annealing, Polycrystalline Si, Hydrogen content,

Dehydrogenation, Glass substrate, Adhesion, Plasma-enhanced CVD

## 1. Introduction

In recent years polycrystalline Si (poly-Si) thin-films formed by post-annealing of amorphous Si (a-Si) have attracted considerable interest as a solar cell material [1-8]. This is because these films show no light-induced degradation due to the absence of a-Si in them; as a result, and less Si material is required compared to a bulk crystalline Si solar cell. These advantages result in the fabrication of high-efficiency and low-cost solar cells. However, high temperature processes used to obtain micrometer-thick poly-Si films, which include epitaxial growth on a seed layer consisting of large-grained poly-Si [4, 5], hour-order furnace annealing [6, 7], and zone melting recrystallization of a-Si films [8], eliminate the possibility of using low-cost substrates. For less thermally resistive substrates such as soda lime glass, we utilize millisecond annealing to sufficiently heat micrometer-thick a-Si films and to avoid thermal damage to glass, which can be realized by flash lamp annealing (FLA). We have already investigated the FLA of 4.5  $\mu\text{m}$ -thick a-Si films prepared by catalytic chemical vapor deposition (Cat-CVD), often called hot-wire CVD (HWCVD), which were deposited on glass substrates with the assistance of a Cr adhesion layer inserted between the a-Si and the glass [9], and reported the fabrication of prototype thin-film solar cells using these poly-Si films [10]. Although we attributed the successful crystallization of the Cat-CVD a-Si films, without serious peeling, to their low hydrogen content as well as the highly adhesive nature of the Cr films, we were unable to determine which of these factors was more important.

In this paper, we have compared the crystallization, by FLA, of a-Si films deposited both by plasma-enhanced CVD (PECVD) and by Cat-CVD with different

hydrogen contents. We have also attempted to crystallize dehydrogenated Cat-CVD a-Si films in order to further understand of effect of the film hydrogen content on the adhesion of a-Si films during FLA.

## 2. Experimental details

Precursor a-Si films with a hydrogen content of about 3% were deposited by Cat-CVD using deposition conditions described previously [11]. Films that were dehydrogenated were heated at 500 °C under a nitrogen atmosphere for 12 h, resulting in a film hydrogen content less than 1%. We also prepared 2.0 μm thick PECVD a-Si films which contained 10% hydrogen; the deposition conditions used were a SiH<sub>4</sub>/H<sub>2</sub> flow ratio of 1/5, a chamber pressure of 2 Torr, and a substrate temperature of 200 °C. These Cat-CVD and PECVD a-Si films were deposited directly onto 20 × 20 × 0.7 mm<sup>3</sup> quartz substrates to check the adhesion of a-Si without a Cr adhesion layer. The surface roughness of the a-Si films was estimated from atomic force microscopy (AFM) images.

One shot of FLA with a fixed pulse duration of 5 ms was performed on each of the a-Si samples, with its irradiance systematically changed by several tens of J/cm<sup>2</sup> by changing the applied voltage of the lamp. Unfortunately, the actual temperature of the Si films during FLA could not be checked due to the lack of *in-situ* measurement systems. The lamp-annealed films were characterized by surface photographs, differential interference microscopy, and Raman spectroscopy.

## 3. Results and discussion

Figure 1 shows surface images of the lamp-annealed Cat-CVD and PECVD Si films which underwent FLA without dehydrogenation. As can be seen, the 1.5- and 3.0- $\mu\text{m}$ -thick a-Si films without dehydrogenation are crystallized under proper irradiance, and are accompanied by partial Si peeling. The 3.0  $\mu\text{m}$  thick a-Si films are crystallized under a lower lamp irradiance than are the 1.5- $\mu\text{m}$ -thick films, because the temperature of the a-Si film achieved during FLA is determined by a balance between generated heat and thermal diffusion of this heat into a substrate. From absorption coefficient arguments, thicker a-Si films absorb more flash lamp light, resulting in more heat generation, while the heat diffusion from the a-Si is rather small for the thicker a-Si films due to the difference in thermal diffusion lengths between the a-Si and the quartz. A more detailed description can be found in our previous paper [11].

Unlike the Cat-CVD films, the PECVD a-Si films show a weaker adhesion to the glass substrates. As also seen in Fig. 1, FLA PECVD a-Si films start to peel off even with a lower irradiance than required for crystallization, which never occurs for the Cat-CVD a-Si films. Figure 2 shows the root-mean-square (RMS) surface roughness of the Cat-CVD and PECVD a-Si films as a function of film thickness. The observed roughness is probably due to the so-called “amorphous-to-amorphous roughening transition”, generally observed on surfaces of a-Si films deposited by Cat- and PECVD [12-14]. Although the estimated roughness is large compared to a previous report [15], this might be due to different deposition conditions. The roughness of the PECVD a-Si surface is larger than that observed for the Cat-CVD a-Si roughness, which might be an indication of its weaker adhesion to glass [15].

Figure 3 shows the surfaces of dehydrogenated Cat-CVD a-Si films after FLA.

No significant peeling can be observed after FLA with relative irradiances of 1.00 and 1.09, under which Si films without dehydrogenation are partially peeled off. This clearly indicates that a-Si films containing less hydrogen show better adhesion to glass substrates during FLA. Clear lateral crystallization features from both edges and spots are seen in the surface photographs of the poly-Si films. A rainbow colored surface, however, does not appear, which is typically observed in the case of films which undergo FLA without dehydrogenation [16]. This might mean that hydrogen atoms in precursor a-Si films are needed for the formation of the 1- $\mu\text{m}$ -pitch grating-like surface structure which enables the observation of the rainbow color. The details of this phenomenon are now under investigation.

Figure 4 shows the Raman spectra of 3.0  $\mu\text{m}$  thick poly-Si films formed by FLA, with the same irradiance, both with and without prior a-Si dehydrogenation. The poly-Si films formed using dehydrogenated a-Si show a crystalline Si (c-Si) peak with a smaller ( $5.2\text{ cm}^{-1}$ ) full width at half maximum (FWHM) and a higher crystallinity than the poly-Si formed without dehydrogenation, which show a FWHM of  $7.6\text{ cm}^{-1}$ ; the latter is in good agreement with that of poly-Si formed on Cr-coated glass [9]. Assuming solid-phase crystallization, these results are quite reasonable, since a more dense material, realized by the removal of hydrogen, gives more chances for Si atoms to change phase (from a-Si to c-Si) via defects [17]. There are, however, disadvantages to the dehydrogenation process and the resultant poly-Si formed. Figure 5 shows differential interference microscopic images of these poly-Si films observed from the backside. Crack-like structures, the formation mechanism of which is presently unclear, are seen only in the image of the poly-Si formed after dehydrogenation. These structures probably deteriorate the film electronic characteristics and the resultant solar

cell performance. In addition, this dehydrogenation requires an hour-order furnace annealing for sufficient removal of hydrogen from the micrometer-thick a-Si films, which completely negates the advantage of FLA for highly productive rapid crystallization. Furthermore, we have also experienced peeling of a-Si films from quartz during the dehydrogenation process even for Cat-CVD a-Si films when the film thicknesses are more than 4  $\mu\text{m}$ . We therefore conclude that as-deposited Cat-CVD a-Si films, essentially containing less hydrogen, are particularly suitable as a precursor material for poly-Si films formed by FLA.

#### **4. Conclusion**

We have shown that a-Si films with lower hydrogen contents show better adhesion to glass during FLA. PECVD a-Si films containing 10% hydrogen start to peel off even for a lamp irradiance lower than that needed for crystallization, and no poly-Si remains after FLA with a higher irradiance, whereas part of the Cat-CVD a-Si films adhere even after crystallization. On the other hand, dehydrogenated Cat-CVD a-Si films show no significant peeling after complete crystallization. Although the poly-Si films formed from dehydrogenated a-Si show a higher crystallinity than those formed from as-deposited Cat-CVD a-Si films, this crystallization is accompanied by the generation of crack-like structures. These facts demonstrate the superiority of Cat-CVD a-Si films as a precursor material for the formation of micrometer-thick poly-Si films by FLA.

#### **Acknowledgments**



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## Figure captions

Fig. 1 Surfaces of Si films prepared by Cat- and PECVD after FLA with various irradiance.

Fig. 2 RMS roughness of a-Si films formed by Cat- and PECVD as a function of film thickness. The line is a guide to the eye.

Fig. 3 Surfaces of dehydrogenated Si films prepared by Cat-CVD after FLA with various irradiance.

Fig. 4 Raman spectra of 3.0  $\mu\text{m}$  thick poly-Si films formed by FLA of a-Si films with and without prior dehydrogenation.

Fig. 5 Differential interference microscopy images of poly-Si films formed by FLA of a-Si films (a) without and (b) with prior dehydrogenation, observed from the glass side.


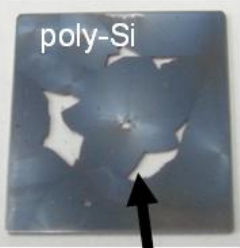

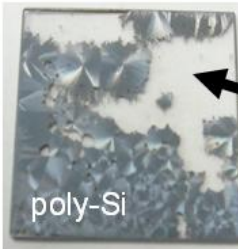
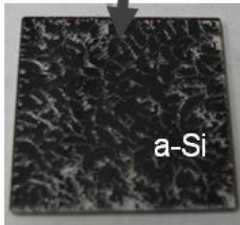


	Relative irradiance			
	0.89	0.97	1.00	1.17
Cat-CVD 1.5 $\mu\text{m}$			 a-Si	 poly-Si ↑
Cat-CVD 3.0 $\mu\text{m}$	partially peeled ↓	 a-Si	 poly-Si ←	peeled ←
PECVD 2.0 $\mu\text{m}$	 a-Si ↓	 peeled	 peeled	

Figure 1 K. Ohdaira *et al.*,

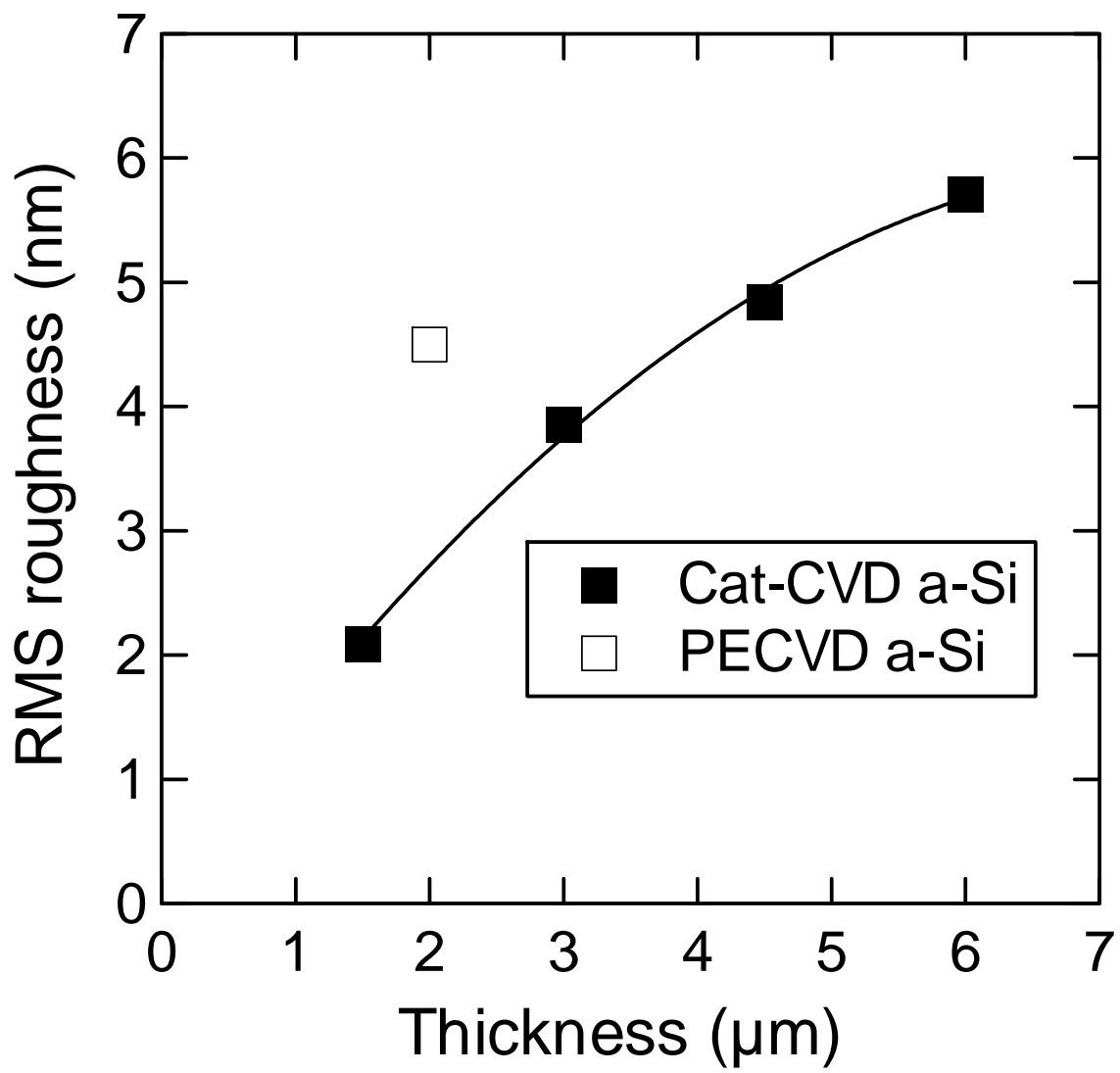


Figure 2 K. Ohdaira *et al.*,

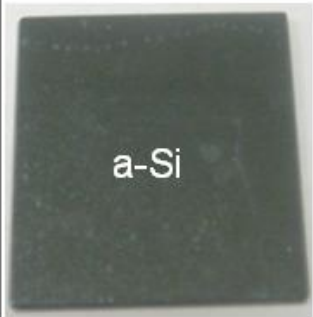
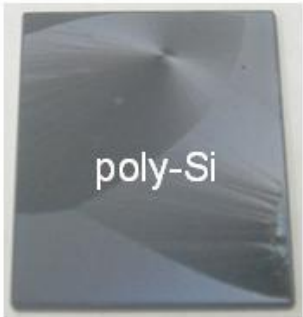

	Relative irradiance		
	0.90	1.00	1.09
Cat-CVD 3.0 $\mu\text{m}$ (dehydrogenated)	 a-Si	 poly-Si	 poly-Si

Figure 3 K. Ohdaira *et al.*,

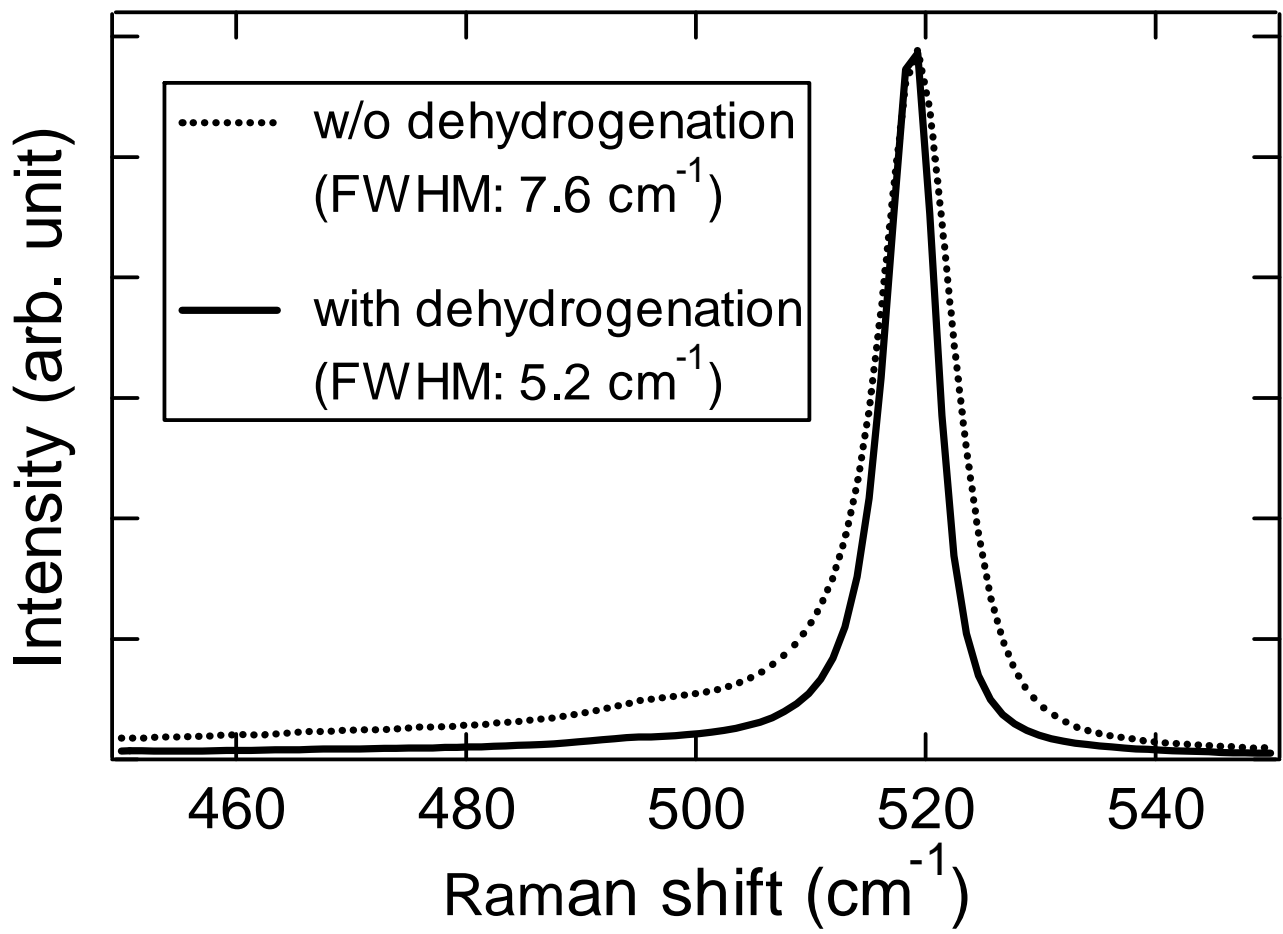


Figure 4 K. Ohdaira *et al.*,



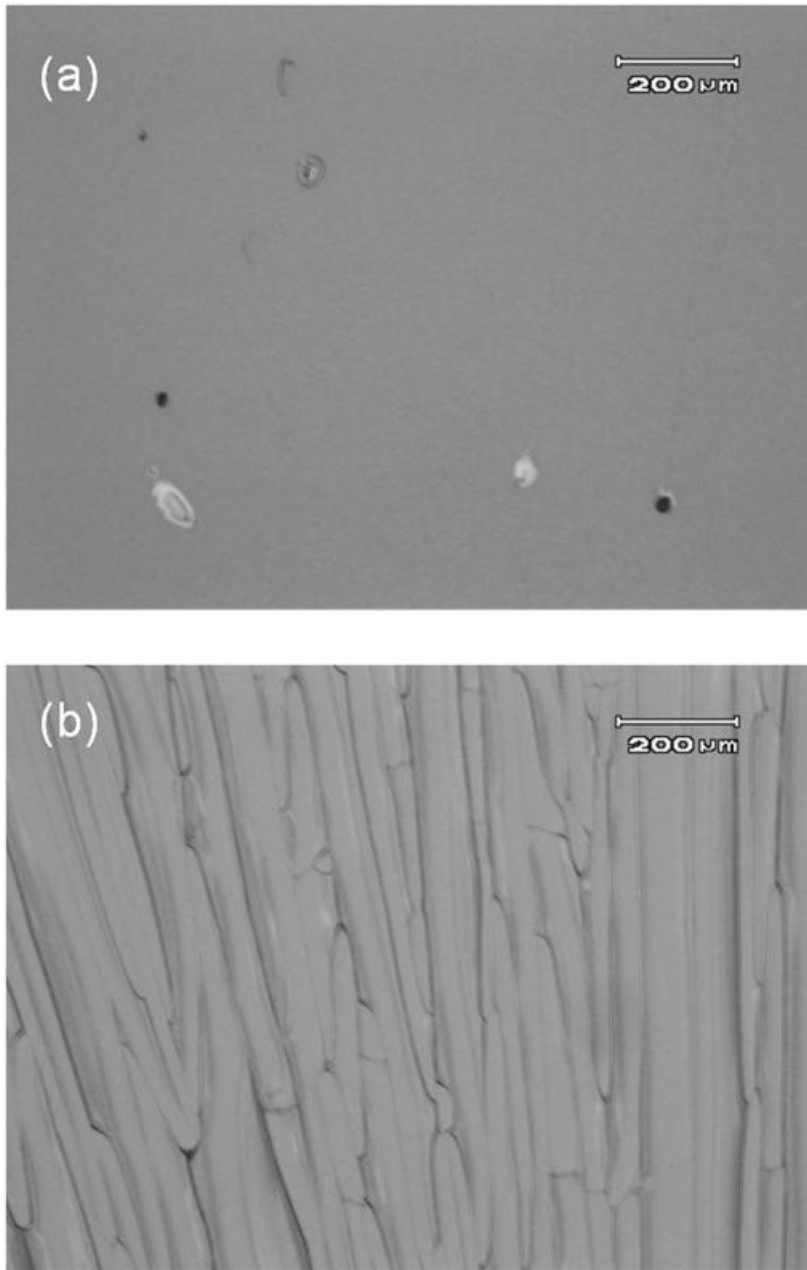


Figure 5 K. Ohdaira *et al.*,