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# Selection of Material for the Back Electrodes of Thin-Film Solar Cells Using Polycrystalline Silicon Films Formed by Flash Lamp Annealing

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Flash lamp annealing (FLA), a rapid annealing technique with a millisecond-order duration, can form polycrystalline silicon (poly-Si) films of a few  $\mu\text{m}$  thickness on glass substrates by crystallizing precursor amorphous Si (a-Si) films without serious thermal damage to the substrates. We attempt to use several kinds of metal films for adhesion layers inserted between the Si films and the glass substrates to prevent Si film peeling during FLA. One of the requirements for the insertion metals is a melting point ( $T_{\text{melt}}$ )

higher than 1414 °C, to which the metal films could be heated during the crystallization induced by FLA. Of the metal films attempted, only Cr films can prevent Si film peeling from soda lime glass substrates, which have a much larger thermal expansion coefficient than quartz, indicating the necessity of sufficient adhesiveness to glass and Si as well as of a high  $T_{\text{melt}}$ . Actual solar cell operation is demonstrated using a flash-lamp-crystallized poly-Si film as an absorber layer and a Cr film as a back electrode.

## 1. Introduction

Thin-film polycrystalline silicon (poly-Si) solar cells have attracted considerable attention because of their effective usage of Si material and high stability against light soaking. High-performance solar cells have been realized using poly-Si films formed on borosilicate glass substrates by the hour-order furnace annealing of precursor amorphous Si (a-Si) films.<sup>1)</sup> Introducing a rapid crystallization technique into the crystallization process will significantly improve the throughput of crystallization. Furthermore, if we choose an appropriate annealing duration, precursor a-Si films can be selectively heated without excess heating of whole glass substrates, which will enable us to use low-cost, low-heat-resistivity substrates such as soda lime glass. We have actually demonstrated that flash lamp annealing (FLA) with a millisecond-order duration can form poly-Si films of more than 4  $\mu\text{m}$  thickness with a crystalline fraction close to unity on glass substrates without serious deformation of the glass substrates.<sup>2,3)</sup> Flash-lamp-crystallized poly-Si films contain spontaneously formed 1- $\mu\text{m}$ -spacing lateral periodic structures with two characteristic regions; fine-grain regions consisting of only 10-nm-sized fine grains formed only through solid-phase crystallization, and large-grain regions having relatively large grains with diameters of a few hundreds of  $\mu\text{m}$  formed partially through melting growth.<sup>4)</sup> The poly-Si films also show

remarkable fundamental properties for solar cell materials such as a long minority carrier lifetime.<sup>5)</sup> A Cr film inserted between a Si film and a glass substrate works as an adhesion film to prevent the peeling of the Si film during FLA.<sup>2,3)</sup> Cr films could also be utilized as back electrodes and back reflectors when the poly-Si films are processed into solar cells. Hence, we should determine the feasibility of using other materials, with better properties such as reflectance and resistivity, for the insertion layer, and also clarify the essential factors for the prevention of Si film peeling. In this study, we have investigated the material dependence of the inserted layers on the prevention of Si film peeling during FLA. We have newly attempted the utilization of Al and Ag films having better optical reflectance than Cr, and of Mo films with a sufficiently high melting point ( $T_{\text{melt}}$ ) of 2623 °C, which would lead to better adhesiveness because the films will not melt during FLA. We have also demonstrated the actual operation of thin-film solar cells fabricated using flash-lamp-crystallized poly-Si films as absorber layers and Cr films, which most effectively prevented Si film peeling in this study, as back electrodes.

## **2. Experimental Procedure**

Figure 1 shows a schematic diagram of a sample structure. Both quartz and soda lime

glass were utilized as substrates. We newly attempted to use Al, Ag, and Mo films as insertion layers between Si films and glass substrates. All the metal films of 60 or 200 nm thickness were formed by sputtering. Precursor a-Si films of 4.5  $\mu\text{m}$  thickness were formed using catalytic chemical vapor deposition (Cat-CVD), which can provide a-Si films with a low film stress and a low hydrogen content, resulting in the formation of a-Si films resistant to peeling during deposition and FLA.<sup>6)</sup> The detailed deposition conditions have been summarized elsewhere.<sup>7)</sup> FLA was performed for a fixed pulse duration of 5 ms, whereas the lamp irradiance was systematically changed (around 20  $\text{J}/\text{cm}^2$ ) to find the optimum conditions. Each sample received only one shot of flash irradiation. No dehydrogenation process was performed prior to FLA. The crystallization and crystalline fraction of the flash-lamp-annealed Si films were characterized by means of Raman spectroscopy.

For the fabrication of solar cells, the surface of the poly-Si films was slightly etched off using  $\text{HF}/\text{HNO}_3$  solution in order to remove a number of voids formed during crystallization. The defect termination of poly-Si absorber layers was then performed by high-pressure water-vapor annealing under the conditions of 1 MPa, 400  $^\circ\text{C}$ , and 10 min prior to the solar cell processes.  $\text{p}^+$ -a-Si films less than 10 nm thick were deposited on stacked structures of defect-passivated intrinsic poly-Si (4  $\mu\text{m}$ )/ $\text{n}^+$ -poly-Si

(10 nm)/Cr (200 nm)/quartz, followed by the formation of surface electrodes consisting of Al and indium tin oxide (ITO) films and by  $2 \times 2$  mm<sup>2</sup>-sized mesa formation using photolithography. The solar cells were characterized by measuring current-voltage (I-V) curves under dark and 1-sun-illuminated conditions.

### 3. Results and Discussion

Figure 2 shows the surfaces of Si films after FLA on quartz substrates with various metal insertion layers. When Al or Ag is inserted, the Si films peel off along with the metal films during FLA in patchy patterns. This is probably because of the low  $T_{\text{melt}}$  values of Al and Ag. The crystallization of a-Si films of a few  $\mu\text{m}$  thickness by FLA progresses laterally from the edges of the samples toward their center, the mechanism of which is based on heat generation due to crystallization, corresponding to an enthalpy difference between a-Si and crystalline Si (c-Si), and the diffusion of the generated heat into neighboring a-Si.<sup>4)</sup> According to this mechanism, the temperature of Si increases up to the melting point of c-Si (1414 °C) at the moment of crystallization.<sup>4)</sup> The inserted metal films, directly in contact with the Si films, could have almost the same temperature as the Si film, which is much higher than the  $T_{\text{melt}}$  of Al of 660 °C or that of Ag of 962 °C. Thus, Al-Al or Ag-Ag bonds could be disconnected during FLA,

resulting in the peeling of the Si films together with the metal layer. In contrast, when a Mo film is inserted, the a-Si film can be converted to a poly-Si film without serious Si and metal film peeling. This seems to be reasonable since the  $T_{\text{melt}}$  of Mo (2623 °C) is much higher than that of c-Si. According to these facts, we need to utilize metal layers with a  $T_{\text{melt}}$  higher than 1414 °C. Figure 3 shows the Raman spectra of poly-Si films formed on Cr- and Mo-coated quartz glass substrates, indicating the formation of poly-Si films with a high crystalline fraction close to unity. There are no significant differences in the peak Raman shift ( $\sim 520 \text{ cm}^{-1}$ ) or line width ( $\sim 7 \text{ cm}^{-1}$ ) between the two crystalline Si signals, which means that the metal layer has no significant effect on crystalline quality.

Figure 4 shows the surfaces of Si films after FLA on soda lime glass substrates with Mo and Cr insertion layers. Unlike in the case of quartz substrates, the Si and the Mo films seriously peel off when a Mo film is inserted between a Si film and a glass substrate. On the other hand, crystallization takes place on a Cr film without serious peeling, as was reported previously.<sup>3)</sup> One possible reason for the more serious film peeling on soda lime glass substrates is the larger thermal expansion. Soda lime glass has a much larger thermal expansion coefficient ( $9.35 \times 10^{-6} / \text{K}$ )<sup>8)</sup> than quartz ( $0.54 \times 10^{-6} / \text{K}$ ).<sup>9)</sup> Metal films are therefore required to have a higher adhesiveness to glass



substrates; otherwise, they would peel off even below their  $T_{\text{melt}}$ . Cr is well known to have excellent adhesiveness to glass,<sup>10)</sup> and one of the possible mechanisms of its high adhesiveness is the existence of an interfacial reaction zone at the glass/Cr interface.<sup>11)</sup> These characteristics might also be true in our samples.

Figure 5 shows the dark and 1-sun-illuminated I-V characteristics of a solar cell fabricated using a flash-lamp-crystallized poly-Si absorber and a Cr back electrode. Rectification and solar cell properties are demonstrated, indicating the feasibility of using Cr films as back electrodes. The series resistances ( $R_s$ ), obtained by analyzing dark I-V characteristics, are not sufficiently low (3-10  $\Omega \text{ cm}^2$ ), part of which would be due to the nonnegligible resistances of the Cr electrodes. The utilization of metal stacking structures, such as Cr/highly conductive metal/Cr, would lead to a decrease in  $R_s$ , resulting in the improvement in the fill factors. Figure 6 shows the external quantum efficiency (EQE) of the poly-Si solar cell. The insufficient EQE in the short-wavelength region would be due to incomplete defect termination of the poly-Si films and/or unoptimized surface and interface passivation, and could be improved by refining solar cell processes. The low EQE in the long-wavelength region would also be related to the insufficient potential of the Cr back reflector. Also from this viewpoint, the fine tuning of the back electrode structure should be performed in the

future.

#### **4. Conclusions**

Cr insertion films have superior ability to suppress the peeling of Si films on glass substrates during FLA. A  $T_{\text{melt}}$  higher than 1414 °C is one of the requirements for insertion metals. Sufficient adhesiveness of metal films to glass substrates is also another requirement, especially when soda lime glass with a large thermal expansion coefficient is utilized as a substrate. We have also demonstrated the actual operation of thin-film poly-Si solar cells, indicating the feasibility of using Cr back electrodes in these cells.

#### **Acknowledgements**

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## Figure captions

Fig. 1. Schematic of the sample structure containing precursor a-Si and metal layers.

Fig. 2. (Color online) Surfaces of Si films after FLA on quartz substrates with various metal insertion layers. The symbols “a”, “c”, and “x” indicate a-Si, c-Si, and peeling parts, respectively.

Fig. 3. Raman spectra of poly-Si films formed on Cr- and Mo-coated quartz glass substrates.

Fig. 4. (Color online) Surfaces of Si films after FLA on soda lime glass substrates with Mo and Cr insertion layers.

Fig. 5. Dark and 1-sun-illuminated I-V characteristics of a solar cell fabricated using a flash-lamp-crystallized poly-Si film and a Cr back electrode.

Fig. 6. EQE of the poly-Si solar cell using a Cr back electrode.

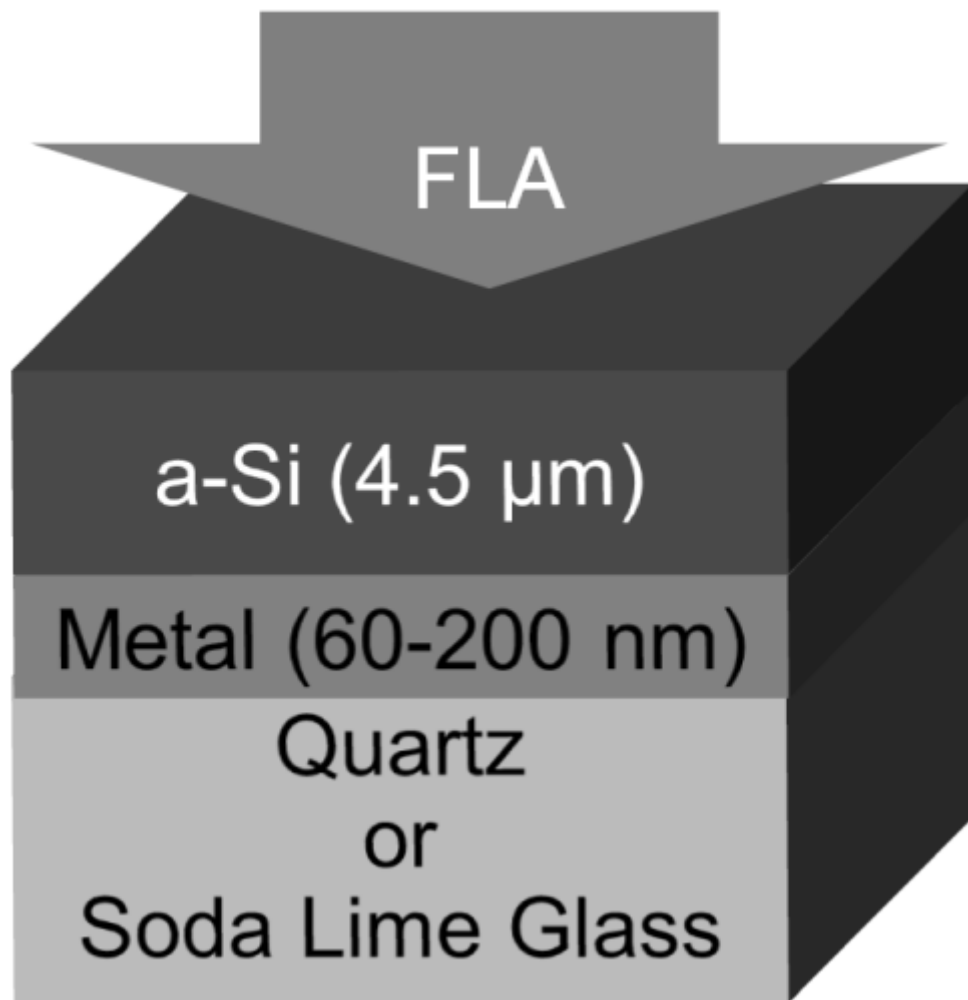


Figure 1 K. Ohdaira *et al.*,

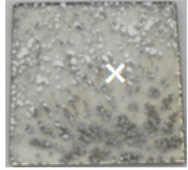



Metal	Al	Ag	Mo	Cr
Surface (20 × 20 mm <sup>2</sup> )				

Figure 2 K. Ohdaira *et al.*,

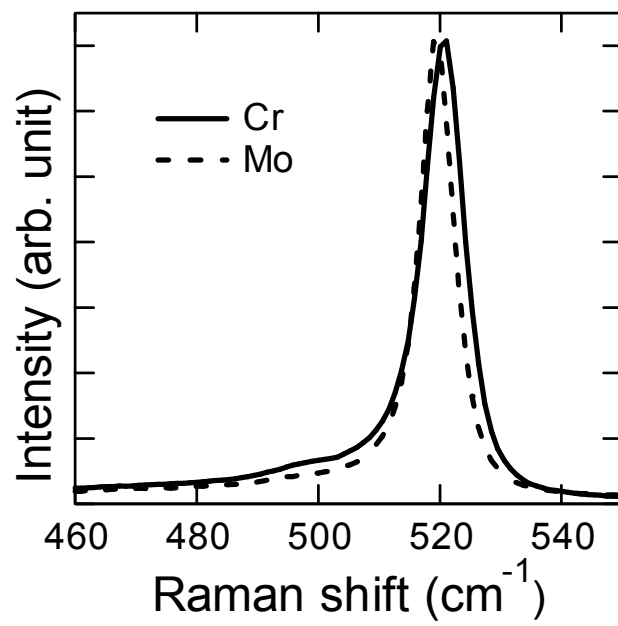


Figure 3 K. Ohdaira *et al.*,





Metal	Mo	Cr
Surface (20 × 20 mm <sup>2</sup> )		

Figure 4 K. Ohdaira *et al.*,

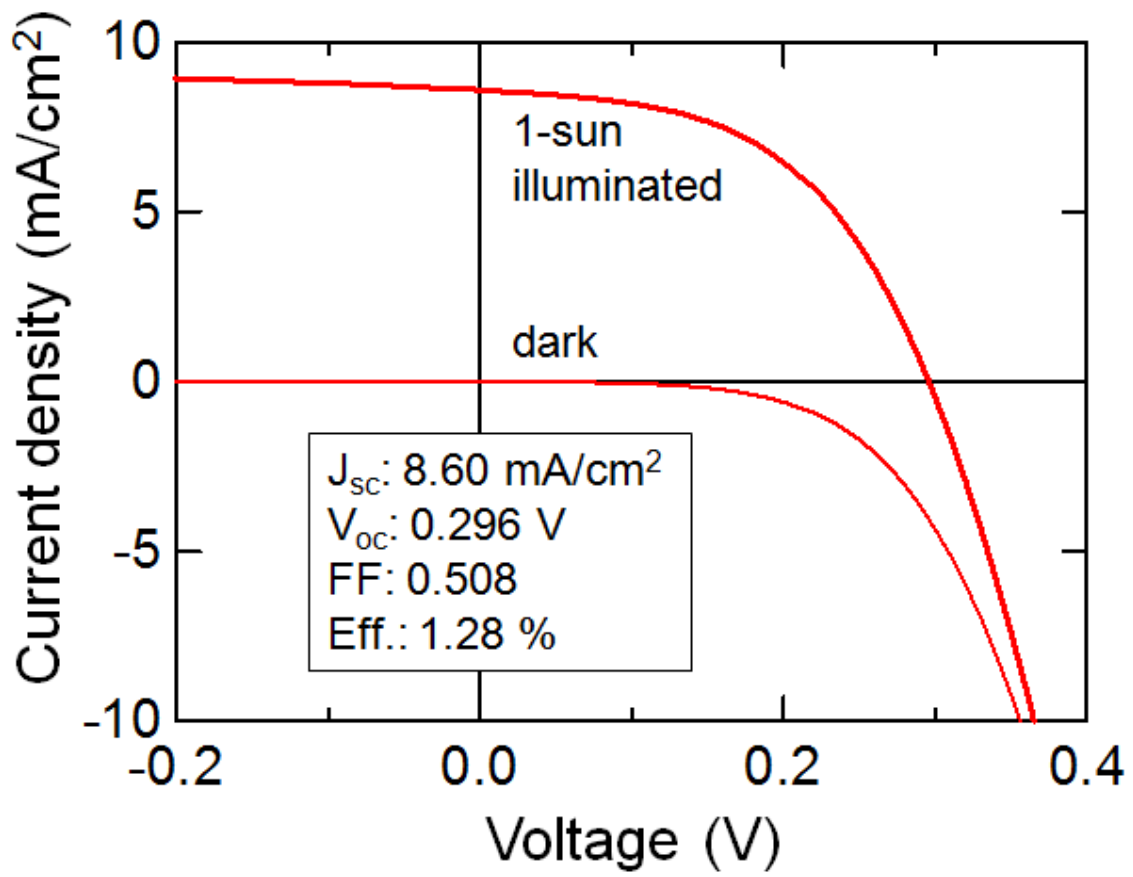


Figure 5 K. Ohdaira *et al.*,

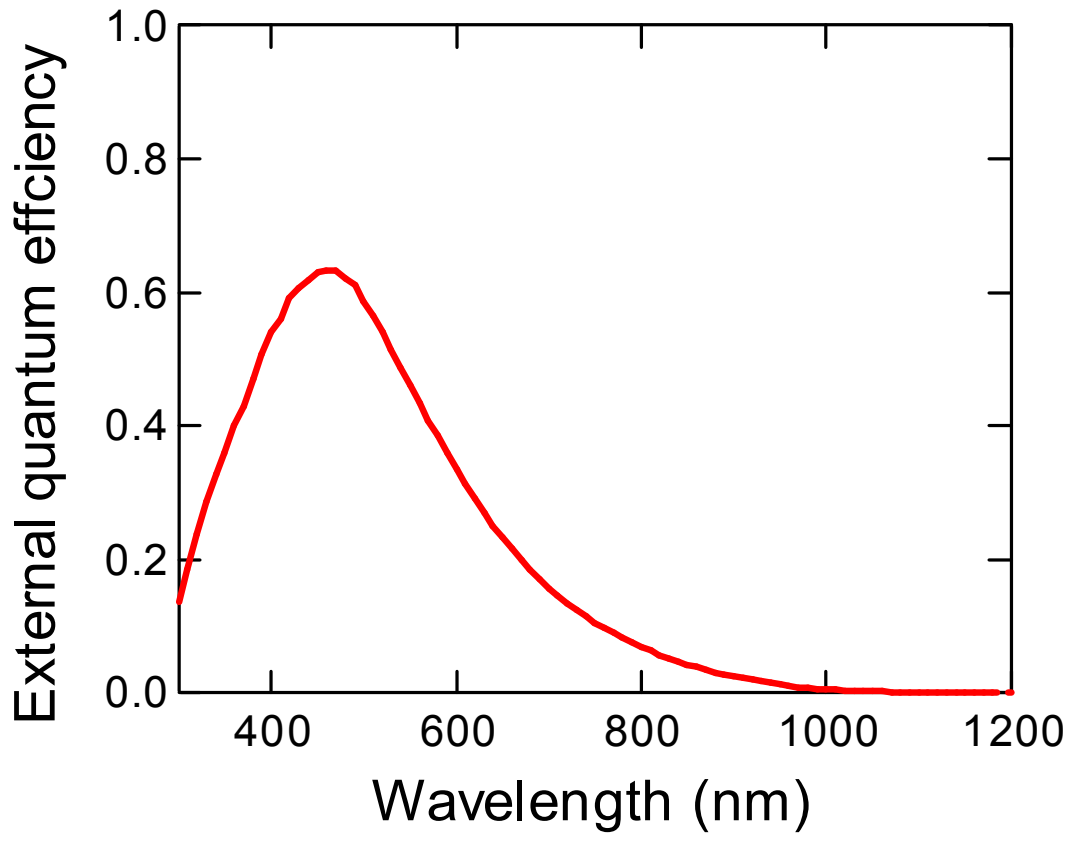


Figure 6 K. Ohdaira *et al.*,