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Description	

Formation of Several-Micrometer-Thick Polycrystalline Silicon Films on Soda Lime Glass by Flash Lamp Annealing

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We have succeeded in forming polycrystalline silicon (poly-Si) films with thicknesses of over 4 μm on soda lime glass by flash lamp annealing (FLA) of precursor amorphous Si (a-Si) films deposited by catalytic chemical vapor deposition (Cat-CVD). The insertion of Cr thin films between glass substrates and a-Si significantly improves the adhesion of Si films to the glass substrates, resulting in uniform crystallization of a-Si in 20 × 20 mm^2 area. Several types of substrate, such as quartz substrates, are also used instead of soda lime glass to elucidate the effects of the properties of glass substrates on formation of the poly-Si films. a-Si films tend to be crystallized under lower irradiance than those on quartz glass substrates, which can be described by the lower thermal conductivity and the thermal diffusion length of soda lime glass. Raman spectra of the poly-Si films on soda lime glass show high crystallinity close to unity. The utilization of soda lime glass with poor thermal resistivity is of great importance for the cost-effective mass production of thin-film poly-Si solar cells.

KEYWORDS: soda lime glass, flash lamp annealing, crystallization, amorphous silicon, polycrystalline silicon, solar cell

1. Introduction

With growing concern about global warming, the widespread use of solar cells is urgently needed, and hence, more cost-effective technologies for the mass production of solar cells are required. Bulk crystalline silicon (c-Si) solar cells, which have a current market share of over 90%,$^{1)}$ are faced with issues of a shortage of Si material and the difficulty in further thinning wafers. From these points of view, thin-film Si solar cells have the advantage of a smaller amount of Si usage, and thus, are more cost-effective solar cells. Amorphous Si (a-Si), microcrystalline Si (μc-Si), and their tandem structures have been commonly used in Si-based thin-film solar cells.$^{2)}$ These solar cells, however, have lower conversion efficiency than c-Si cells because of their shorter carrier diffusion length, which results in limitation of film thickness at the sacrifice of optical absorption. To overcome this issue, a considerable number of studies have been conducted on the formation of high-quality polycrystalline Si (poly-Si) films by post-annealing of precursor a-Si films formed on glass substrates or by epitaxial growth on a large-grained poly-Si seed layer.$^{3-7)}$ The most advanced studies are based on furnace annealing aimed at the solid-phase crystallization (SPC) of a-Si at temperatures lower than the melting points of the glass substrates.$^{6)}$ Although fabrication of poly-Si solar cells with conversion efficiencies of over 10% has been demonstrated, this solar cell relies on an hour-order annealing process with disadvantages in mass production. Epitaxial growth of poly-Si on seed layers has to overcome an issue of trade-off between thermal damage to the substrates and improvement of poly-Si quality with sufficient thermal treatment. Rapid crystallization processes under nonthermal equilibrium conditions can realize the selective heating of a precursor a-Si film without heating the entire substrates. Excimer laser annealing (ELA) is one of the most widely utilized nonthermal equilibrium treatments, particularly for the formation of submicron-thick poly-Si films.8, 9) However, since it has a pulse duration of several tens of ns, corresponding to the thermal diffusion length of a-Si of less than 1 μm, it is not suitable for the crystallization of micrometer-order-thick a-Si for solar cell application. For the sufficient heating of such thick a-Si films without complete heating of the glass substrate, millisecond-order treatment is required, which can be performed by plasma jet crystallization (PJC)10-16) and flash lamp annealing (FLA).17-27) We have demonstrated that 4.5-μm-thick poly-Si films with high areal uniformity can be formed on quartz substrates with only one shot of flash irradiation without any prior dehydrogenation of precursor a-Si films prepared by catalytic chemical vapor deposition (Cat-CVD).19) We have also clarified that the insertion of Cr films between Si films and glass substrates effectively suppresses the peeling of Si films during FLA.19) This

Cr insertion is not for the enhancement of metal-induced crystallization but for the enhancement of the adhesion of Si films onto the substrates.23) Because the inserted Cr films can be utilized as back electrodes and reflectors, substrate-type thin-film p-i-n poly-Si solar cells can be realized on glass substrates by the simultaneous crystallization of stacked p-i-n a-Si films. Considering the actual cost-effective fabrication process for solar cells using these poly-Si films, utilization of cheaper glass substrates is necessary, the glasses of which usually have inferior characteristic variables such as a lower liquidus temperature and a larger thermal expansion coefficient, indicating further difficulties for the uniform areal crystallization without peeling of Si films.

In this study, we have attempted to form poly-Si films on soda lime glass substrates by FLA of 4.5-μm-thick a-Si. The effect of Cr films on the suppression of Si peeling and their thickness dependence has been particularly investigated. We demonstrate that several-micrometer-thick poly-Si films can be formed on soda lime glass with a lower irradiance of FLA than quartz substrates.

2. Experimental Procedure

The composition of the soda lime glass used in this study and the characteristic variables of soda lime glass, quartz, and a-Si are summarized in Tables I and II,27-31) respectively. Cr films of 60 and 200 nm thickness were first formed by sputtering on the soda lime glass substrates of 20 × 20 × 0.7 mm^3, followed by deposition of 4.5-μm-thick a-Si films by Cat-CVD under a pressure of 1.1 Pa at a deposition rate of approximately 100 nm/min. To confirm the adhering effect of Cr, structures without Cr films were also prepared as control samples. The hydrogen content of the Cat-CVD a-Si of about 3% is much lower than that of a-Si prepared by conventional plasma-enhanced CVD (PECVD), which enables us to skip the dehydrogenation prior to FLA. Only one shot of flash irradiation was applied to each sample, the pulse duration of which was about 5 ms. Lamp irradiance with several tens of J/cm^2 was systematically varied and is mentioned as relative irradiance owing to the lack of precise measurement methods for it. Annealed Si films were characterized by surface photographs and differential interference microscopy images. The crystallization of Si films and their crystallinity were characterized by Raman spectroscopy using a He-Ne laser with a wavelength of 632.8 nm.

3. Results and Discussion

Figure 1 shows the surfaces of structures without Cr films after FLA. Under relative lamp irradiance of 1.00, no significant change in surface morphology can be observed and no c-Si phase is confirmed in the Raman spectrum, while the Si film is completely peeled off under a higher relative irradiance of 1.07. Although lamp irradiance was systematically varied, we cannot find any suitable conditions for the crystallization of a-Si without peeling in this structure. Soda lime glass loses about 5 mg of weight together with Si films during FLA, the weight of which corresponds to their thickness of about 3.5 μm. This phenomenon can be understood as the increasing temperature of the Si/glass interface above the liquidus temperature of soda lime glass of about 1005 °C[28)] and resulting in the peeling of the surface part of the glass together with Si during FLA. The thermal diffusion lengths (L_T) of a-Si and soda lime glass in 5 ms are on the order of several tens of μm. The total thickness of the Si and the missing part of the glass is less than the L_T, and hence, the hypothesis of the partial peeling of the glass is acceptable.

Figure 2 shows the surfaces of Si films on Cr-coated soda lime glass substrates after FLA. Unlike the cases without Cr films, serious peeling of a Si film is suppressed, indicating excellent adhesion of the Cr film to the soda lime glass and to Si.[32-34)] After FLA, with a relative lamp irradiance of 0.97, of the sample with inserted Cr films of 60 nm thickness, a-Si is partially crystallized from the edges of the sample towards the center, the crystallization of which has also been similarly confirmed in the case of quartz substrates.[19)] Under a higher relative irradiance of 1.01, however, Si film is partially peeled off although the a-Si component completely disappears with crystallization. On the other hand, in the structure with a 200-nm-thick Cr film, complete crystallization of 20 × 20 mm^2 area has been realized under a relative irradiance of 1.01, indicating better adhesion of Cr to the glass and to the Si. Note that no crystallization occurs under almost the same relative irradiance in the absence of Cr insertion, which is due to the effective reflection of irradiated light at the Cr surface. The thickness dependence of the adhesion, however, cannot be described simply on the basis of the high adhesion of Cr film to Si that must be determined only by a property of the Cr/Si interface. The compensation of the thermal expansion of substrates by Cr films with a large linear thermal expansion coefficient, previously discussed in the case of quartz substrates19), also cannot describe this phenomenon because the linear thermal expansion coefficient of soda lime glass is higher than those of a-Si and c-Si41), unlike in the case of quartz. One possible reason for the improved adhesion is that Cr films work as thermal baths, which tend to ease the excessive heating of the glass surface. The use of thicker Cr film results in a larger thermal capacity, and thus a lower glass temperature must be realized. Detailed numerical investigations on thermal diffusion during FLA should be performed to further understanding this phenomenon.

The Si surfaces on Cr-coated quartz substrates are also summarized for comparison in Fig. 2. Complete crystallization in a 20 × 20 mm^2 area can be seen under a relative lamp irradiance of 1.07, as has already been reported.[19)] It should be noted that a-Si films on quartz substrates require higher lamp irradiance for complete areal crystallization. This phenomenon can be described by the difference in thermal conductivity between soda lime and quartz glasses. The maximum temperature of Si during FLA is determined on the basis of the balance of the total generated heat in the Si layer by optical absorption and their thermal diffusion into the substrate.[18)] In this case, the total generated heat in the Si layer is the same under the same irradiance because of the same initial a-Si film thickness as well as the same Cr film thickness working for optical reflection. On the other hand, quartz has a longer thermal diffusion length than soda lime glass at almost all the temperatures relating to FLA, as shown in Fig. 3.[35-40)] This difference causes more effective confinement of generated heat in the Si layer on soda lime glass than on quartz, resulting in complete areal crystallization under lower lamp irradiance.

Figure 4 indicates Raman spectra of poly-Si films on soda lime glass with a 200-nm-thick Cr film. A typical Raman spectrum from a poly-Si film formed on a quartz substrate is also shown for comparison. A clear c-Si peak located at 520 cm^{-1}

can be observed, whereas no significant signal relating to a-Si can be observed at approximately 480 cm^{-1}. A full width at half maximum (FWHM) of the c-Si peaks is estimated to be 7-9 cm^{-1}, which indicates the existence of grains of about 7-8 nm in size.[42) This characteristic Raman spectrum can also be observed in the entire 20 × 20 mm^2 area. These Raman features are similar to those of poly-Si films formed on quartz substrates[19). An optical microscopy image of the poly-Si film formed on soda lime glass is shown in Fig. 5, indicating characteristic periodic structures with a pitch of about 1 μm spontaneously formed perpendicular to the lateral growth direction, which act as optical gratings, resulting in a rainbow colored surface. The root mean square (RMS) of the surface roughness determined by atomic force microscopy is about 120 nm, which is similar to that of the poly-Si films formed on quartz substrates.[22) Note that 4.5-μm-thick a-Si films on Cr-coated soda lime glass substrates are crystallized by the same crystallization mechanism as the case on quartz substrates, and the formed poly-Si indicates an equivalent crystallinity close to unity. These findings demonstrate the feasibility of the formation of thin-film poly-Si solar cells on soda lime glass using Cr film, which act not only to prevent peeling of Si films but also as a back contact and a back reflector in actual device structures.

4. Conclusions

The 4.5-μm-thick a-Si films deposited by Cat-CVD on soda lime glass substrates are crystallized by FLA. Peeling of Si films and soda lime glass surfaces, which is observed in the structures without Cr films, is suppressed by the insertion of Cr films, resulting in uniform crystallization in a 20 × 20 mm^2 area. The poly-Si films formed on soda lime glass substrates reveal high crystallinity close to unity, which is equivalent to those formed on quartz substrates. Characteristic periodic structures appear on the surface of the poly-Si after FLA, indicating a crystallization mechanism similar to the case on quartz substrates. These findings demonstrate the sufficient feasibility of soda lime glass as a substrate for poly-Si films formed by FLA.

Acknowledgments

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Table I Composition of soda lime glass used in this study.

Oxides	Concentration (wt%)
SiO_2	71
Na_2O	13
CaO	9
MgO	4
Al_2O_3	2
K_2O	1

Table II Liquidus temperature (melting points) and linear thermal expansion coefficient of soda lime and quartz glasses and a-Si.

	Liquidus temperature (°C)	Linear thermal expansion coefficient (10^{-6}/K)
Soda lime	1005 28)	9.35 28)
Quartz	1670 29)	0.54 30)
a-Si	1145 27)	4.4 31)

Figure captions

Fig. 1. Surfaces of samples with soda lime glass substrates without insertion of Cr films after FLA with various lamp irradiances.

Fig. 2. Surfaces of samples with soda lime glass substrates with 60- and 200-nm-thick Cr films after FLA with various lamp irradiances. Surfaces using quartz substrates treated under various lamp irradiances are also summarized for comparison.

Fig. 3. Thermal diffusion length of quartz and soda lime glasses as a function of temperature estimated using the equation of $L_T = \sqrt{\kappa t / c\rho}$, where κ is thermal conductivity, t treatment duration of 5 ms, c heat capacity, and ρ density.

Fig. 4. Raman spectra of poly-Si formed on Cr-coated soda lime and quartz glass substrates.

Fig. 5. Differential interference microscopy image of a poly-Si surface formed on Cr-coated soda lime glass.

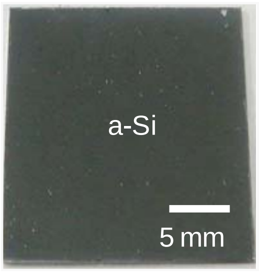
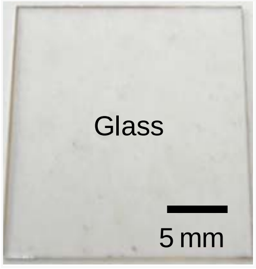
Relative irradiance	1.00	1.07
		

Figure 1 K. Ohdaira *et al*.,

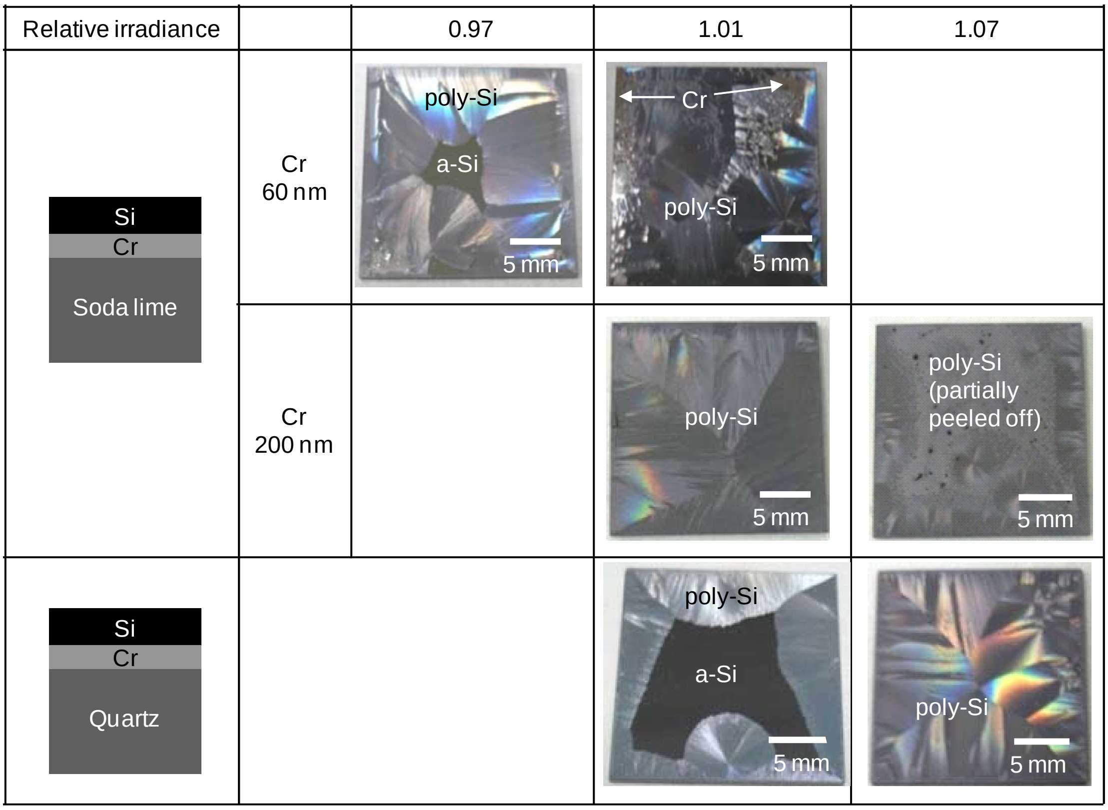


Figure 2 K. Ohdaira *et al.*,

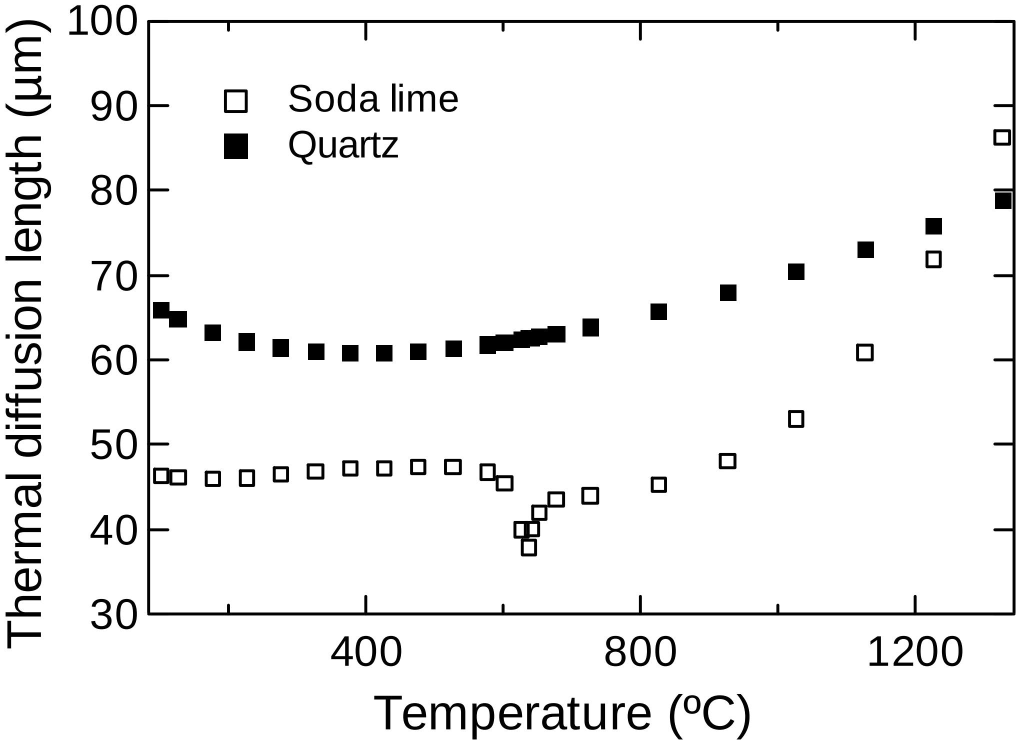


Figure 3 K. Ohdaira *et al*.,

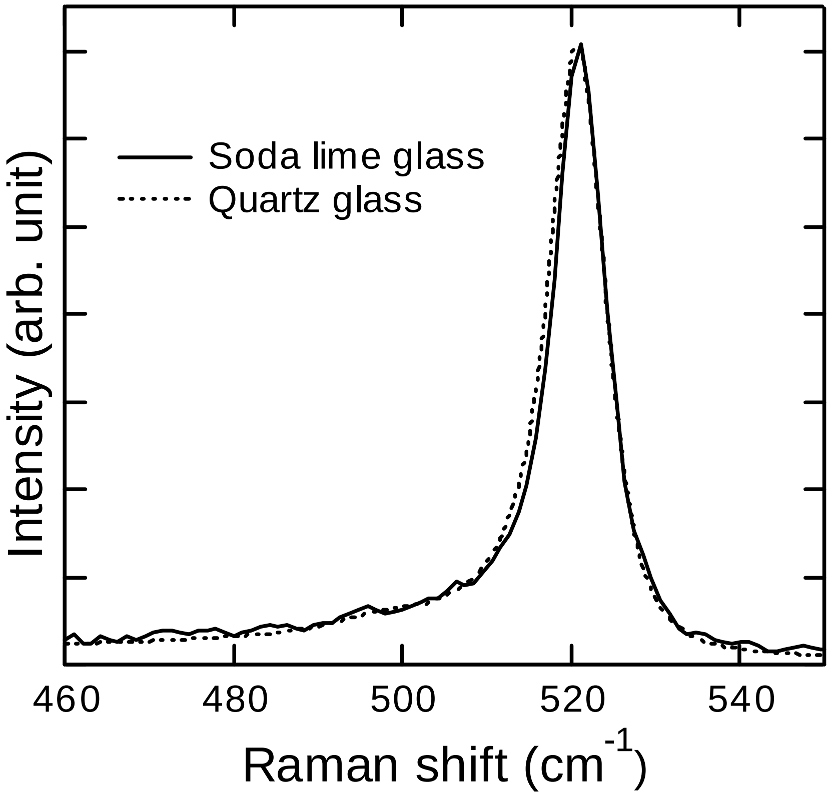


Figure 4 K. Ohdaira *et al.*,

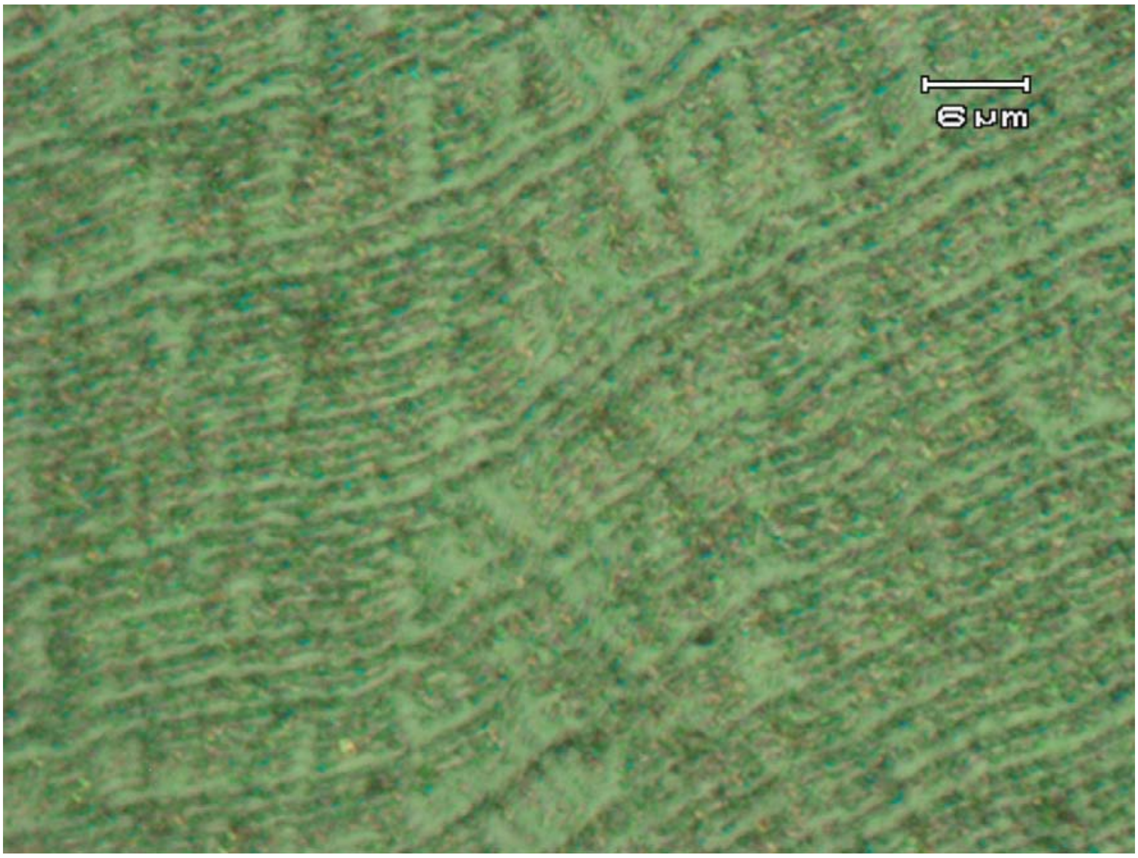


Figure 5 K. Ohdaira *et al*.,