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Defect Termination of Flash-Lamp-Crystallized Large-Grain Polycrystalline Silicon Films by High-Pressure Water Vapor Annealing

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1. Introduction

Thin-film polycrystalline silicon (poly-Si) has attracted considerable interest as a photovoltaic material because of the low amount of Si usage and high stability against light soaking. The crystallization of precursor amorphous Si (a-Si) films prepared on low-cost substrates through annealing process is one of the most promising approaches to obtain poly-Si films. Of a variety of annealing techniques, we have investigated flash lamp annealing (FLA), millisecond-order discharge from Xe lamps. Due to its proper annealing duration, one can crystallize μm-order-thick a-Si films by a single shot of flash pulse without serious damage onto glass substrates. We have so far confirmed that more than 4 μm-thick poly-Si films can be formed on glass substrates by FLA [1,2]. The crystallization induced by FLA is based on explosive crystallization (EC), lateral crystallization driven by the release of latent heat. We have observed various types of ECs [3,4], and EC governed by liquid-phase epitaxy (LPE) occurs when electron-beam-(EB-) evaporated a-Si films are used as precursors, resulting in the formation of poly-Si films with relatively large grains [5,6]. Unlike flash-lamp-crystallized (FLC) poly-Si films formed from chemical-vapor-deposited (CVD) hydrogenated a-Si films [7], FLC poly-Si films contain few hydrogen atoms, and effective defect termination process is required to obtain poly-Si films with low defect density. In this study, we have performed high-pressure water vapor annealing (HPWVA) to FLC poly-Si films formed from EB-evaporated a-Si films. HPWVA is a defect-terminating annealing technique, developed by Sameshima *et al.*, in which samples are heated under high-pressure water vapor atmosphere [8]. The effectiveness of HPWVA for the defect termination of thin (<100 nm) poly-Si films has well been confirmed [9]. Our aim to apply HPWVA is to reduce the defect density of thick (>1 μm) poly-Si films for solar cell application.

2. Experimental procedures

Intrinsic 3-μm-thick a-Si films were deposited by EB evaporation directly on 20×20×0.7 mm^3 quartz glass substrates. We then performed flash lamp annealing to each sample at a fluence of 10 J/cm^2 and a stage heating temperature of 500 °C under Ar atmosphere. Only one shot of flash irradiation was supplied for each sample. Crystallization and crystalline fraction of Si films after FLA was characterized by Raman spectroscopy.

HPWVA was then performed to FLC poly-Si films under a pressure of 0.2-1.0 MPa at 350-500 °C for 3 h. The dangling bond density of FLC poly-Si films were characterized by electron spin resonance (ESR). The hydrogen content of precursor EB-evaporated a-Si films was checked by secondary ion mass spectrometry (SIMS).

3. Results and discussion

Figure 1 show the SIMS profile of hydrogen atoms in a precursor EB-evaporated a-Si film. Only small amount of hydrogen on the order of 10^{19} /cm^3 is incorporated in the a-Si film, which is two orders of magnitude lower than that in hydrogenated catalytic CVD (Cat-CVD) a-Si films [7].

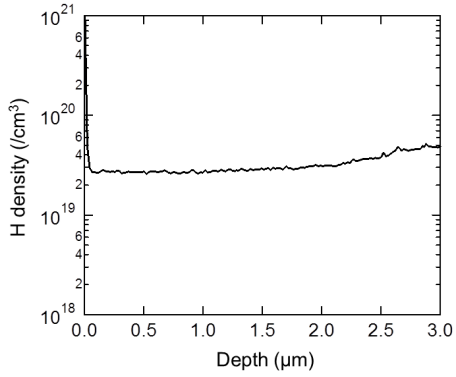

Fig. 1 SIMS profile of hydrogen atoms in EB-evaporated a-Si film.

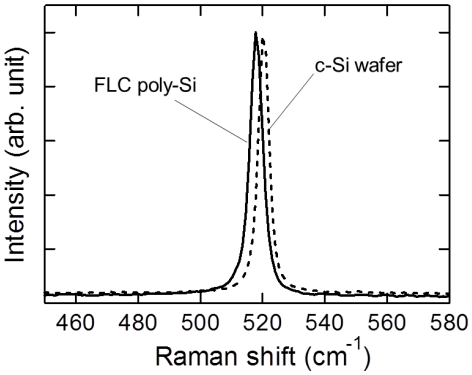

Fig. 2 Raman spectrum of a FLC poly-Si film formed from an EB-evaporated a-Si film. The spectrum of a c-Si wafer is also shown for comparison.

We thus cannot expect defect termination by hydrogen atoms in Si films.

Figure 2 shows a typical Raman spectrum of a FLC poly-Si film formed from an EB-evaporated a-Si film. A clear peak originating from crystalline Si (c-Si) phase is seen, while no signal from a-Si phase can be observed. This indicate that poly-Si with high crystalline fraction is formed by a single shot of flash pulse. We have also already confirmed that the FLC poly-Si films formed consist of grains stretching along lateral EC directions with a length of several tens of μm and a height and width of a few hundred nm [5,6].

Figure 3 shows an example of the ESR spectra of FLC poly-Si films before and after HPWVA. We can clearly see reduction in ESR spin density, indicating the effectiveness of HPWVA for FLC poly-Si films. Figure 4 shows ESR spin density of FLC poly-Si films after HPWVA at various temperatures. The defect density of the FLC poly-Si films before HPWVA is ~3.5×10^{17} /cm^3, which is much smaller than that of FLC poly-Si films formed from unhydrogenated sputtered a-Si films [10]. This is probably because of larger grain size and consequent smaller number of grain boundaries in FLC poly-Si films formed from EB-evaporated a-Si films. As HPWVA temperature increases, the defect density of the poly-Si decreases more significantly, and becomes one third of the original defect density at an annealing temperature of 500 °C. Since the defect density of poly-Si films after annealing in inert gas is unchanged, decrease in defect density is considered to be the effect of high-pressure water vapor. HPWVA for the FLC poly-Si films is, however, less effective than that for 50-nm-thick laser-crystallized poly-Si films, whose defect density reaches 1×10^{17} /cm^3 after HPWVA at 310 °C [9]. Most likely reason for this is the difference of poly-Si thickness, and HPWVA under higher pressure would lead to more effective reduction in dangling bonds of thick FLC poly-Si films. The defect termination process is expected to enhance the performance of solar cells fabricated using FLC poly-Si films.

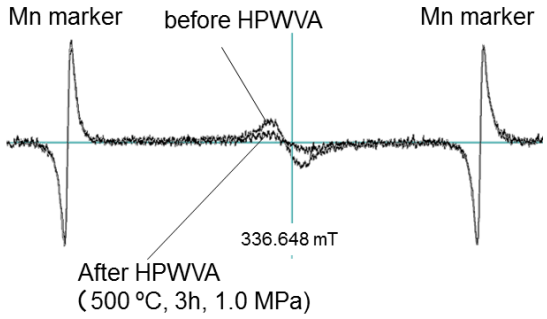

Fig. 3 An example of ESR spectra of FLC poly-Si films formed from EB-evaporated a-Si films before and after HPWVA.

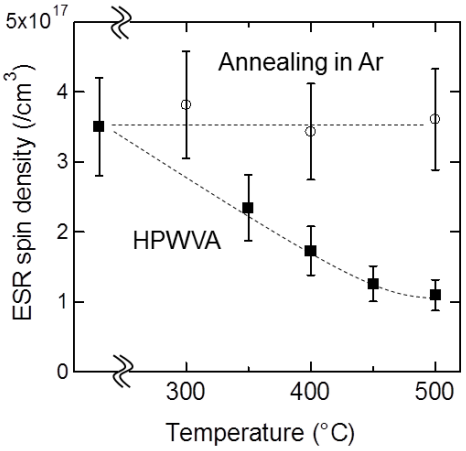

Fig. 4 ESR spin density of a FLC poly-Si film formed from an EB-evaporated a-Si film as a function of HPWVA temperature. The spin density of poly-Si films after annealing under Ar atmosphere is also plotted for comparison. Dashed lines are guides to the eye.

3. Summary

HPWVA can decrease the defect density of FLC poly-Si films with a thickness of 3 μm formed from EB-evaporated a-Si films. HPWVA at higher temperature results in more effective defect termination, and a FLC poly-Si film with a defect density of 1×10^{17} /cm^3 is obtained by HPWVA at 500 °C.

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References

[1] K. Ohdaira, Y. Endo, T. Fujiwara, S. Nishizaki, and H. Matsumura, Jpn. J. Appl. Phys. **46** (2007) 7603.

[2] K. Ohdaira, T. Fujiwara, Y. Endo, S. Nishizaki, and H. Matsumura, Jpn. J. Appl. Phys. **47** (2008) 8239.

[3] K. Ohdaira, T. Fujiwara, Y. Endo, S. Nishizaki, and H. Matsumura, J. Appl. Phys. **106** (2009) 044907.

[4] K. Ohdaira, N. Tomura, S. Ishii, and H. Matsumura, Electrochem. Solid-State Lett. **14** (2011) H372.

[5] K. Ohdaira and H. Matsumura, J. Cryst. Growth (in press).

[6] K. Ohdaira, K. Sawada, N. Usami, S. Varlamov, and H. Matsumura, Jpn. J. Appl. Phys. (in press).

[7] K. Ohdaira, H. Takemoto, K. Shiba, and H. Matsumura, Appl. Phys. Express **2** (2009) 061201.

[8] T. Sameshima and M. Satoh, Jpn. J. Appl. Phys. **36** (1997) L687.

[9] K. Asada, K. Sakamoto, T. Watanabe, T. Sameshima, and S. Higashi, Jpn. J. Appl. Phys. **39** (2000) 3883.

[10] K. Ohdaira, S. Ishii, N. Tomura, and H. Matsumura, J. Nanosci. Nanotech. **12** (2012) 591.