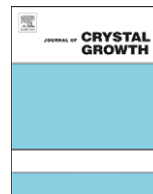




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# Crystallographic properties of grain size-controlled polycrystalline silicon thin films deposited on alumina substrate

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## ABSTRACT

In order to obtain higher performance of polycrystalline silicon (poly-Si) thin film devices, crystallinity of poly-Si thin films should be enhanced. In this study, poly-Si thin films with thickness of 10 μm heading for the solar cell application were thermally deposited onto alumina substrates with in-situ grain size controlling by using the intermittent source gas supply method to reduce grain boundaries. By changing source gas supply condition, the grain size was controlled in the range of a few μm to over 10 μm. Improvement of crystallinity of poly-Si thin films could be observed with grain size enlargement. The peak position and width of Raman TO–LO peak at around 520 cm<sup>−1</sup> of small-grained sample showed larger shift from ideal value of c-Si, but becoming closer to c-Si with grain size enlargement, indicating stress relaxation. In photoluminescence measurement, intensity of TO–BE peak which indicates the crystallinity increased with grain size enlargement. These crystallinity improvements with grain size enlargement resulted in increasing of carrier mobility of poly-Si thin films from 20 to 40 cm<sup>2</sup>/V s.

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## 1. Introduction

Polycrystalline silicon (poly-Si) thin film is one of the most promising materials for many kinds of devices such as thin film transistors or thin film solar cells with many advantages of lower material cost than bulk silicon and higher electronic properties than amorphous materials. However, the performance of poly-Si thin film devices, in other words the carrier transport property, is strongly influenced and limited by crystallographic defects mainly at grain boundaries. Particularly, in solar cell device, crystallographic defects crucially deteriorate the photovoltaic performance because they act as recombination centers of photo-generated carriers [1]. In addition, the formation of poly-Si thin films onto foreign low-cost substrates such as ceramics or glasses, in spite of the biggest advantage of poly-Si thin film, will induce further defects resulted from thermal stress by the difference of thermal coefficient between silicon thin film and substrate through processing.

In order to decrease the influence of crystallographic defects, especially grain boundaries, grain size enlargement is one proper answer. In this study, poly-Si thin films with thickness of 10 μm heading for the solar cell application were thermally deposited at 1100 °C onto alumina substrates with direct grain size controlling

by using the intermittent source gas supply method [1–3]. Grain size enlargement of poly-Si thin films was investigated from the point of view of the crystallinity, i.e., the amount of crystalline disorder, and electronic property.

## 2. Experimental procedure

As substrates, commercially available polycrystalline alumina (Al<sub>2</sub>O<sub>3</sub>, 99.9%) substrates as true foreign substrates and reference single-crystalline silicon wafers were applied. Before the deposition of poly-Si thin films, SiO<sub>2</sub> thin layers with the thickness of 500 nm were formed by plasma enhanced chemical vapor deposition (PE-CVD) as intermediate buffer layers, which would prevent some metal impurities diffuse from substrates into poly-Si thin films. Onto these substrates, p-type poly-Si thin films were deposited by thermal CVD at atmospheric pressure [1–3]. SiH<sub>2</sub>Cl<sub>2</sub> (DCS), BCl<sub>3</sub>/Ar (100 ppm) and H<sub>2</sub> were used as source gas, doping gas and carrier gas, respectively. The deposition method consists of two stages: the first-step for nucleation at 1000 °C and the second-step for deposition at 1100 °C with high deposition rate of about 0.6–0.7 μm/min. To control the silicon nucleation density, the intermittent supply of source gas was introduced in the first-step. Fig. 1 shows the flow sequence of DCS in the first-step. The period of one cycle is represented as *T* and the DCS flowing time is represented as *D*. In this work, the intermittent ratio *D/T* is defined and varied from 100% to 10% by changing *D* from 10 to 1 s with *T*

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fixed to 10 s. The total time of  $D$  was adjusted to 3 min by changing the number of cycles; e.g., 30 times for  $D/T$  of 60% and 180 times for  $D/T$  of 10%. After the first-step, poly-Si thin films were deposited on the nucleation-controlled substrates in the second-step by continuous source gas supply. The film thickness and hole concentration were adjusted around  $10\text{ }\mu\text{m}$  and  $10^{17}\text{ cm}^{-3}$ , respectively. Also, direct deposition of poly-Si thin films in the same condition as second-step mentioned above without first-step was performed (denoted as 1 step).

To characterize crystallinity of poly-Si thin films prepared as above, X-ray diffraction (XRD) measurement with  $\text{CuK}\alpha$  radiation, Raman scattering spectroscopy with excitation by Ar laser at 514 nm, photoluminescence (PL) at 7 K with excitation wavelength 980 nm at  $40\text{ mW/cm}^2$  power, and Hall effect measurement were performed.

### 3. Results

Fig. 2 shows plane view images of poly-Si thin films on alumina substrates deposited with different intermittence ratio  $D/T$ . Grain size of poly-Si thin films was successfully controlled by

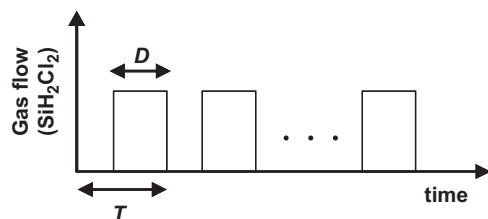


Fig. 1. The flow sequence of DCS in the first-step. The period of one cycle is represented as  $T$ , and the flowing time of DCS in one cycle is represented as  $D$ .

the intermittent gas supply method, showing almost the same tendency in case of silicon substrates [1]. It can be clearly observed that the grain size was enlarged from 3–5 to 15–20  $\mu\text{m}$  with reducing intermittent ratio  $D/T$  from 100% to 10%, while grain size in case of 1 step deposition was very small (2–3  $\mu\text{m}$ ). Average thickness of each film was almost the same at  $10\text{ }\mu\text{m}$ , so the effective grain size for device application once or twice as film thickness could be obtained directly in deposition process by using the intermittent source gas supply method.

Fig. 3 shows the ratio of (220)/(111) diffraction intensities of poly-Si thin films with different grain size from XRD measurement. With an increase of the grain size, intensity of (220)

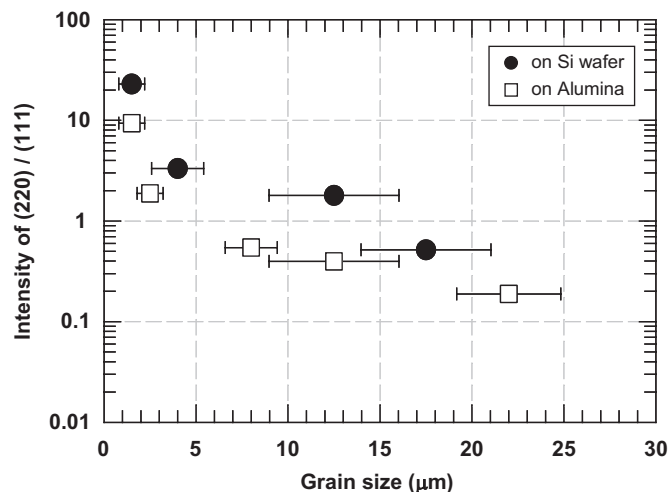


Fig. 3. Intensity ratio of (220)/(111) of poly-Si thin films with different grain size silicon and alumina substrates.

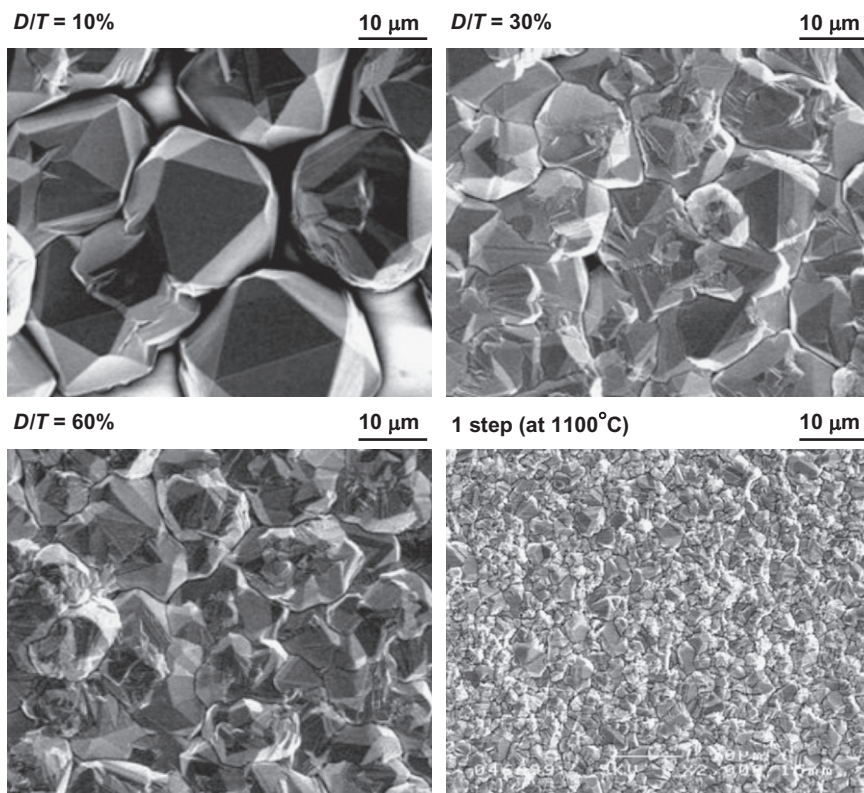


Fig. 2. Surface image of poly-Si thin films on alumina substrates deposited by different intermittence ratio  $D/T$ .

preferential orientation decreased and (111) orientation dominated the crystal orientation in poly-Si with the biggest grain size. Fig. 4 shows lattice constant calculated from XRD data. Lattice constant was also influenced by enlargement of grain size of poly-Si thin films on alumina substrates, while it was almost the same regardless of the grain size in on-silicon case. The lattice constant

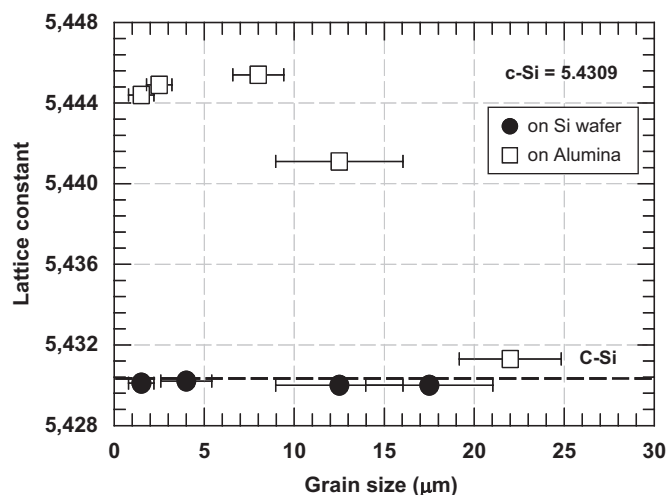


Fig. 4. Lattice constant of poly-Si thin films with different grain size on silicon and alumina substrates.

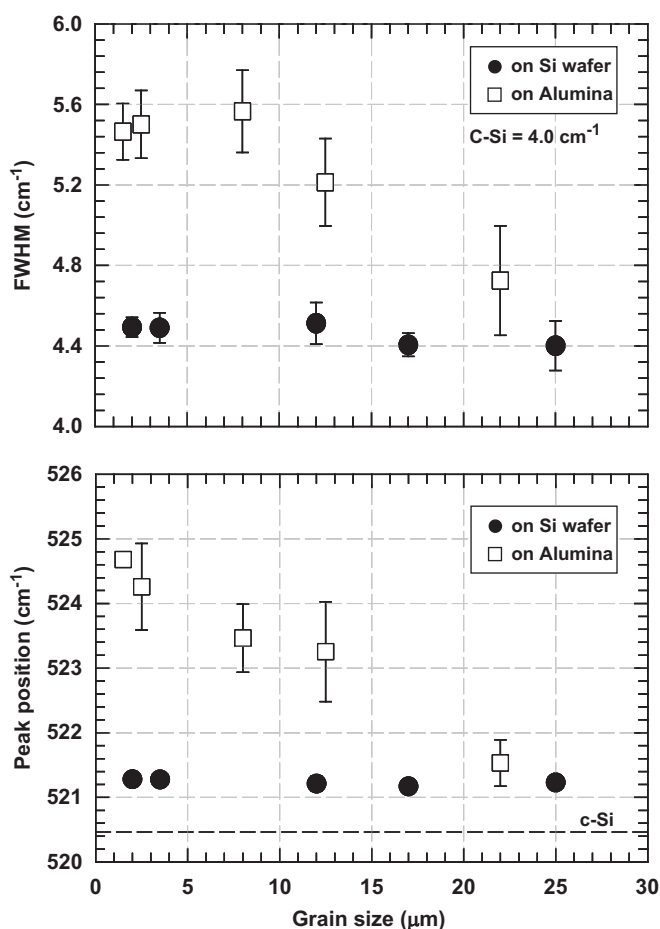


Fig. 5. Full-width at half-maximum (FWHM) and peak position of Raman peaks of poly-Si thin films with different grain size on silicon and alumina substrates.

of poly-Si thin films on alumina substrates showed large shift from crystalline silicon (c-Si) value in case of small grain size and was dramatically improved with an increase of grain size, becoming closer to that of c-Si.

Fig. 5 shows the result of Raman scattering measurement; full-width at half-maximum (FWHM) and peak position of the TO-LO phonon band (at  $520.5\text{ cm}^{-1}$  in c-Si) as a function of the grain size. Peak position and FWHM of poly-Si thin film with small grains on alumina substrate were shifted to higher wave number ( $524.5\text{ cm}^{-1}$ ) and became broader ( $5.5\text{ cm}^{-1}$ ). With an increase of grain size, FWHM and peak position of the TO-LO phonon band were drastically shifted to those of c-Si values, just the same tendency as lattice constant from XRD. Even in case of poly-Si thin films on silicon substrates, the slight shift of FWHM and peak position from c-Si and improvement by grain size enlargement were observed.

Figs. 6 and 7 show PL spectra of the poly-Si thin films with different intermittent ratio  $D/T$  (different grain size) deposited onto silicon and alumina substrates, respectively. All PL spectra are normalized by peak intensity of the tail-to-tail part (around  $0.95\text{--}1.0\text{ eV}$ ). The most remarkable feature is the difference of peak at around  $1.08\text{ eV}$  among samples. This peak represents transverse optical (TO) phonon replica of the bound excitons (BE) at boron atoms [4], and in the case of silicon substrates, started to appear and increased with the grain size enlargement. Moreover, peak position of TO-BE peak became closer to that of c-Si ( $1.092\text{ eV}$ ) with an increase of the grain size. In addition, peak at around  $1.12\text{ eV}$  which is related to transverse acoustic (TA) phonon replica of BE could be observed in poly-Si thin film on silicon with the largest grain size. On the other hand, poly-Si thin films on alumina substrates showed no TA-BE peaks and very small TO-BE peak only in the case of biggest grain size. This tendency of peak appearance and sharpening with grain size enlargement was also seen in so-called D1 peak (around  $0.80\text{ eV}$ ) which is related to dislocations. As one more interesting thing in the case of alumina substrates, large shift of peak position of tail-to-tail peak to higher energy ( $0.926\text{--}0.986\text{ eV}$ ) was observed with an increase of grain size.

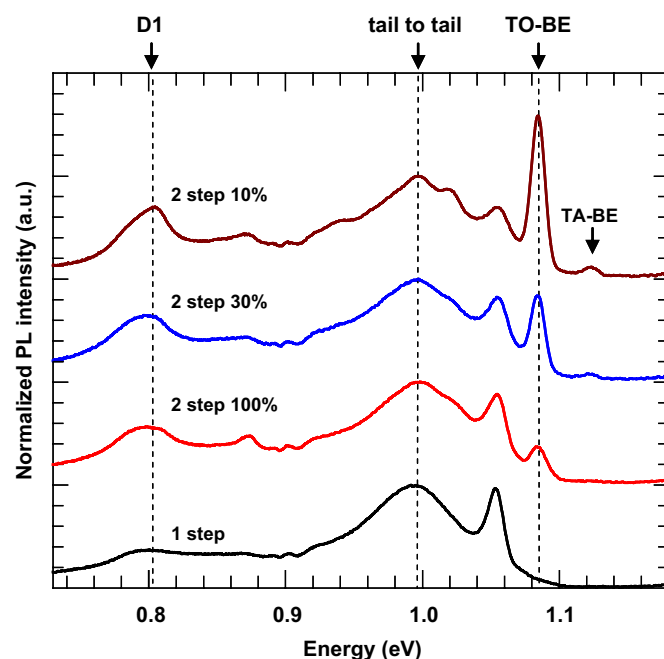


Fig. 6. Photoluminescence spectra of poly-Si thin films deposited on silicon substrates.

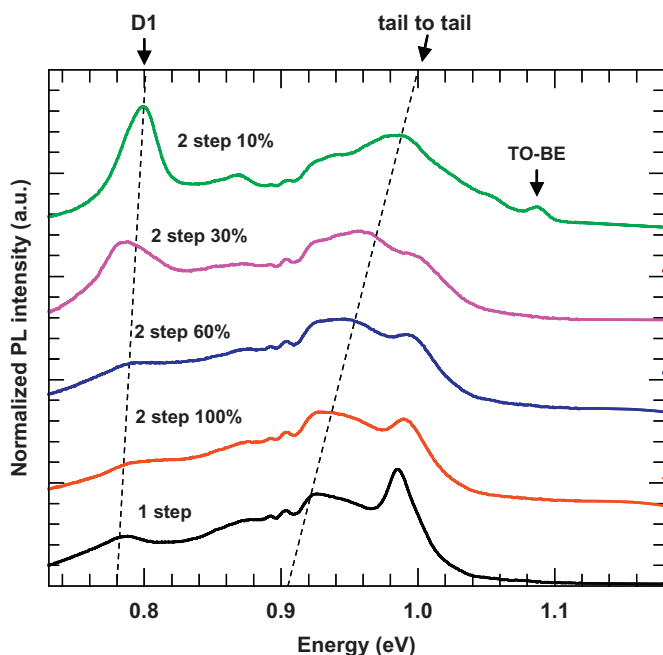


Fig. 7. Photoluminescence spectra of poly-Si thin films deposited on alumina substrates.

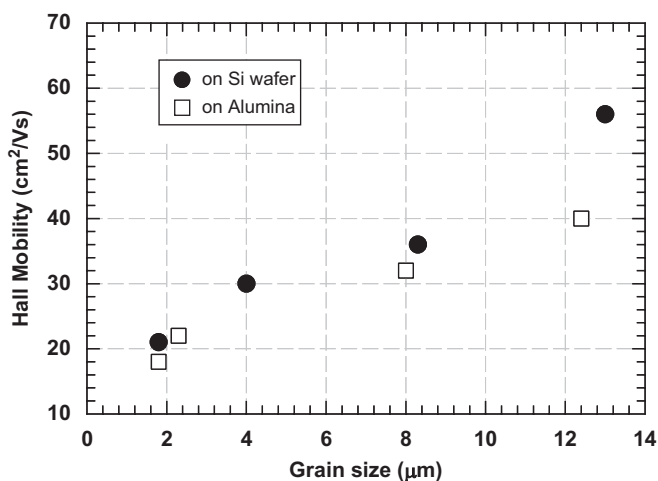


Fig. 8. Hall mobility of poly-Si thin films with different grain size on silicon and alumina substrates.

Fig. 8 shows Hall mobility of poly-Si thin films as a function of the grain size. With an increase of the grain size, Hall mobility was improved from 20 to 60 cm<sup>2</sup>/Vs in case of silicon substrates and from 20 to 40 cm<sup>2</sup>/Vs in the case of alumina substrates.

#### 4. Discussion

By using the intermittent source gas supply method, grain size of poly-Si thin films was controlled in the range of a few μm to over 10 μm. This mechanism is explained as follows. At the initial stage of deposition, silicon clusters adhere onto substrate to form silicon nuclei in source gas supplying time, and some of unstable nuclei are to be etched away by HCl or H<sub>2</sub> during intermission time. Therefore, smaller intermittent ratio (longer intermission time) causes smaller amount and density of silicon nuclei finally remained onto the substrate. Grain size depends on the lateral space each nucleus has to grow, so can be enlarged by nucleation

density reduction realized by decreasing the intermittent ratio. Fig. 3 explains that (111) plane is more stable to etching than (220) plane relating to the difference of surface energy [3].

The result of XRD and Raman scattering measurement showed the same tendency. Poly-Si thin film with small grains on alumina substrate gave very large shift from ideal c-Si value and became closer to c-Si with grain size enlargement. The shifts of these values from c-Si indicate the large internal compressive stress and large amount of disorders in poly-Si thin films on alumina. The internal stress would be caused by the difference of thermal expansion coefficient. The theoretical thermal stress ( $\sigma_{th}$ ) due to the different thermal expansion coefficients is given by

$$\sigma_{th} = E(\alpha_1 - \alpha_2)(T_{low} - T_{high})/(1 - \nu)$$

where  $E$  is the Young's modulus,  $\alpha_1$  and  $\alpha_2$  are the thermal expansion coefficients of different materials,  $T_{low}$  and  $T_{high}$  are low and high temperature in process, respectively, and  $\nu$  is the Poisson's ratio [5,6]. The calculated thermal stress was around 1.1 GPa during temperature cycles from 1100 °C to room temperature and calculated internal stress of small-grained poly-Si thin film on alumina substrate from the shift of Raman TO-LO peak was almost the same value. Grain size enlargement can be said to be effective not only to grain boundary reduction but also to internal stress relaxation, resulting in crystallinity improvement within the grains. This is probably due to the reduction of interaction between grains such as collision.

PL result reflects the crystallinity related to photo-generated carrier's activity, so it is very important for photovoltaic application. The appearance, sharpening and position shift of TO-BE, TA-BE, D1 and tail-to-tail peaks can be used to judge the crystalline quality of poly-Si thin films, because they will be shifted to lower energy and broadened by residual strain which results from dislocations and point defects [4,7–11]. In the case of poly-Si thin films on silicon substrates, TO-BE peak clearly increased with grain size enlargement as shown in Fig. 6, confirming the crystallinity improvement in agreement with Raman and XRD results. Large shift to lower energy of tail-to-tail peak and difficulty of appearance of other peaks in poly-Si thin films with smaller grains on alumina substrates explained poor crystallinity due to large stress discussed above, but grain size enlargement could be the help or must be applied to improve the crystallinity.

The crystallinity improvement by grain size enlargement was also reflected in the Hall mobility increasing, because the mobility of majority carriers in poly-Si thin film would be largely dominated by the carrier scattering at the potential barriers due to defects especially at grain boundaries [1]. Hall mobility of poly-Si thin films on silicon substrates was larger than that of poly-Si thin films on alumina substrates in spite of almost the same grain size, due to the fact that the poly-Si thin films on alumina substrates had deep tail states. For the photovoltaic application, the relationship between crystallographic defects and minority carrier transport property should be investigated in further study.

#### 5. Conclusions

Grain size of poly-Si thin films deposited on silicon or alumina substrates was enlarged by the intermittent source gas supply method over 10 μm. Poly-Si thin films on alumina substrates have larger compressive stress caused by difference of the thermal expansion coefficients between alumina substrates and silicon thin films. XRD, Raman, PL measurement proved that with an increase of grain size on alumina substrates, crystalline disorder and stress were improved with stronger degree than in the case of poly-Si thin films on silicon substrates. As a result, Hall mobility of

poly-Si thin films even deposited on alumina substrates was increased from 20 to 40 cm<sup>2</sup>/V s. It can be concluded that enlargement of grain size is essential in order to achieve good electronic properties of poly-Si thin film-based devices.

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