Fabrication of (111)-oriented Si layers on SiO$_2$ substrates by an aluminum-induced crystallization method and subsequent growth of semiconducting BaSi$_2$ layers for photovoltaic application

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We have prepared (111)-oriented Si layers on SiO₂ (fused silica) substrates from amorphous-Si(a-Si)/Al or Al/a-Si stacked layers using an aluminum-induced crystallization (AIC) method. The X-ray diffraction (XRD) intensity from the (111) planes of Si was found to depend significantly on growth conditions such as the thicknesses of Si and Al, deposition order (a-Si/Al or Al/a-Si on SiO₂), deposition technique (sputtering or vacuum evaporation) and exposure time of the Al layer to air before the deposition of Si. The crystal orientation of the Si layers was confirmed by 0-2θ, 2θ XRD and electron backscatter diffraction (EBSD). The photoresponse properties of semiconducting BaSi₂ films formed on the (111)-oriented Si layers by the AIC method were measured at room temperature. Photocurrents were clearly observed for photon energies greater than 1.25 eV. The external quantum efficiencies of the BaSi₂ were also evaluated.

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1. Introduction

Novel Si-based materials are of great interest for high-efficiency solar cells. At present, most solar cells produced are bulk silicon based. However, the band gap of Si is only 1.1 eV, which is approximately 0.3 eV smaller than the ideal band gap for solar cells from the viewpoint of the solar spectrum [1]. In addition, the optical absorption coefficient ($\alpha$) of Si is much smaller than that of GaAs and CdTe. Thus, a Si thickness of at least 100 $\mu$m is required to form crystalline Si solar cells. For this reason, we have focused on orthorhombic barium disilicide (BaSi$_2$) as an interesting and useful alternative material to Si. Both experimental and theoretical studies have revealed that BaSi$_2$ has a very large $\alpha$ value of over $10^5$ cm$^{-1}$ at 1.5 eV [2,3]. This value is more than two orders of magnitude larger than that of crystalline Si. In addition, by replacing half of the Ba atoms with isoelectric Sr atoms, the band gap of BaSi$_2$ was found to reach the ideal value of approximately 1.4 eV, matching the solar spectrum [2,4]. Thus, BaSi$_2$ has attracted significant attention for use in solar cells. The purpose of the present study was to fabricate BaSi$_2$ layers on SiO$_2$ (fused silica) and to investigate its photoresponse properties with regard to application to inexpensive solar cells. For this purpose, the aluminum-induced crystallization (AIC) was employed [5-7]. AIC is a metal induced crystallization (MIC) [8] technique that enables low-temperature crystallization of amorphous Si (a-Si) below the eutectic temperature of 577 °C, and leads to large grained poly-Si layers. Recently, Knaepen et al. have studied the crystallization kinetics of the MIC process in detail.
for 20 different metals [9]. A preferential (111) orientation of the Si layers was reported [10]. This is favorable for the subsequent growth of BaSi$_2$ layers, because $a$-axis-oriented BaSi$_2$ films can be epitaxially grown on Si(111) with a lattice mismatch of approximately 1% [11-15]. However, the growth of (100)-oriented Si layers has been also reported [16-18].

In this study, the influence of the layer thicknesses of Si and Al, deposition order (a-Si/Al or Al/a-Si on SiO$_2$), deposition technique (sputtering or vacuum evaporation) and exposure time of the Al layer to air before the deposition of Si on the crystalline quality of the Si layers was investigated. The photoresponse properties of polycrystalline BaSi$_2$ films grown on (111)-oriented poly-Si layers prepared by the AIC method on SiO$_2$ substrates were also studied. There have been no reports on the photoresponse properties of BaSi$_2$ until very recently; these properties are very important when we discuss quantum efficiency in BaSi$_2$. In a previous paper [19], we reported the external quantum efficiency in 900-nm-thick BaSi$_2$ epitaxial films for the first time.

2. Experimental procedure

First, the influence of the layer thicknesses and deposition order of Al and Si on the crystallization behavior of AIC-Si layers was investigated. The AIC process was performed as follows. Al layers were deposited on SiO$_2$ by radio-frequency (RF) magnetron sputtering, followed by breaking of the vacuum to form a native Al oxide layer for 50 h, and the
subsequent deposition of a-Si layers by RF magnetron sputtering. The thickness of Al was varied from 50 to 300 nm. The thickness of the Si was almost the same as that of the Al. The vacuum level was 1.0 Pa and the RF power was 100 W. The deposition rates of Al and Si by RF magnetron sputtering were approximately 50 and 25 nm/min, respectively. The deposition order of Al and Si was inverted for sample E. Samples were annealed in a dry N₂ ambient atmosphere at 500 °C for 10 h. During annealing, a-Si was transformed to the crystal phase by exchange between the Al and a-Si layers. The preparation method for samples A-E is summarized in Table 1. We next investigated the influence of the deposition technique (sputtering or vacuum evaporation) on the crystalline quality of the AIC-Si layers. First, a 100 nm-thick Al layer was deposited, followed by breaking of the vacuum to form a native Al oxide layer for 10 min, and the subsequent deposition of a 100-nm-thick a-Si layer. For the vacuum evaporation of Al, conventional resistive heating using a tungsten filament was employed, and the deposition rate of Al was approximately 100 nm/min. For the vacuum evaporation of Si, an electron-beam evaporation was used, and the deposition rate was approximately 3 nm/min. The samples were annealed in a dry N₂ ambient atmosphere at 500 °C for 10 h. As described later, the crystalline quality of AIC-Si layers depends on exposure time of the Al layer to air. The exposure time of 10 min was chosen here just to shorten the time necessary for this experiment. The preparation method for samples F-J is summarized in Table 2. BaSi₂ layers for photoresponse measurements were prepared as
follows. After the Al layers were etched away, the wafers were dipped in a hydrofluoric acid to remove native oxide layers of Si, followed by heating at 550 °C for 5 min in ultra high vacuum. Then, approximately 30-nm-thick Si layers were grown by molecular beam epitaxy (MBE), and approximately 300-nm-thick undoped BaSi$_2$ layers were subsequently grown. The growth procedure employed for the preparation of the BaSi$_2$ layers was almost the same as that adopted previously [19]. Finally, Al was evaporated on the surface to form 1.5-mm-spacing striped electrodes. The ohmic nature of the contacts was confirmed from the current-voltage characteristics. The samples were not covered with anti-reflection coatings.

The crystalline quality of the films was characterized by $\theta$-$2\theta$ and $2\theta$ X-ray diffraction (XRD) using a Cu $K\alpha$ source, atomic force microscopy (AFM) and scanning electron microscopy (SEM). Electron backscatter diffraction (EBSD) was performed in order to analyze the preferential orientation of the film. The X-ray beam was incident at an angle of 2 ° in the $2\theta$ XRD measurement. Both the $\theta$-$2\theta$ and $2\theta$ XRD measurements help us understand what lattice plane in the crystal is parallel to the substrate plane. The photocurrent in the lateral direction between the electrodes was evaluated at RT by a lock-in technique using a xenon lamp with a 25-cm focal-length single monochromator (Bunko Keiki, SM-1700A). The light intensity was calibrated using a pyroelectric sensor (Melles Griot, 13PEM001/J).
3. Results and discussion

3.1 Formation of (111)-oriented Si layers on SiO$_2$ by AIC

Figure 1 shows the $\theta$-2$\theta$ and 2$\theta$ XRD patterns of samples A-E. The Al layers were not etched for these measurements. The (111) peaks of Si were observed in the $\theta$-2$\theta$ XRD patterns for samples A-C, but were not found in the 2$\theta$ XRD patterns. Thus, these results show that (111)-oriented Si layers were fabricated in samples A-C. The peak intensity of Si(111) was found to increase with increasing thickness of the Si layers. However, layer exchange, and hence the crystallization of Si, was not observed for sample D. We believe that much longer annealing times are required for sample D because of the thicker Si layer. In sample E, prepared by inverted AIC, the layer exchange occurred and a poly-Si layer was formed on the top surface and a metallic Al layer was formed between the poly-Si layer and the SiO$_2$ substrate, which can act as a back electrode for solar cells. In addition, a very flat surface was obtained in this sample. The root-mean-square (RMS) roughness of sample E was much smaller than that of sample B, prepared by the standard AIC method, as shown in Fig. 2. However, the peak intensity of the Si(111) plane was much smaller in sample E, at about 100 counts. We believe that whether the crystallization of Si occurs or not is much more important than the RMS roughness value of the AIC-Si surface, because a flat surface can be produced later by epitaxial thickening of the AIC layers. Thus, we chose to use the standard AIC process from here on.
Next, we investigated the influence of the deposition method on the crystalline quality. Figure 3 shows the $\theta$-2$\theta$ and 2$\theta$ XRD patterns of samples F-J, where the Al and Si layers were deposited by either RF magnetron sputtering or vacuum evaporation. The thicknesses of the Al and Si layers were kept constant at 100 nm. The sample preparation method is summarized in Table 2. Layer exchange was found to occur in all of the samples.

As shown in Fig. 3, intense peaks from Si(111) and Al(111) planes were observed for samples H-J, with the peak intensity being much larger in sample J. These results show that the vacuum evaporation of Al layers significantly improves the crystalline quality of AIC-Si layers. To further investigate the influence of the Al deposition method, AFM observations were performed just after Al deposition and after 50 h exposure to air for sample B, and just after Al deposition and after 48 h exposure to air for sample J. As shown in Fig. 4, it was found that the Al had a much smoother surface and its grain size was much smaller in the vacuum-evaporated Al layer. In the case of vacuum evaporation, the kinetic energy of Al atoms is approximately $k_B T (< 1 \text{ eV})$, where $k_B$ and $T$ are the Boltzmann constant and the absolute temperature, respectively. In contrast, the kinetic energy of Al atoms sputtered is on the order of 10 eV [20]. We think that this difference is attributed to the difference in surface roughness shown in Fig. 4. It is well known that the presence of native Al oxide at the a-Si/Al interface plays an essential role in the final crystal quality of poly-Si layers [5-7, 21-24]. We believe that the rough surface of the Al layers produced by sputtering gave rise to
non-uniform Al oxide layers, which influenced the crystallization of the AIC-Si layers. Figure 5 shows the dependence of the XRD peak intensity of the Si(111) plane on the air-exposure time of the vacuum-evaporated Al layers. The AIC process conditions were the same as those of sample J except for the exposure time. The peak intensity tended to increase with increasing exposure time, although there is a lack of values in the intermediate time range. On the basis of these results, we adopted the AIC process of sample J, on which BaSi$_2$ films were grown by MBE.

Figures 6(a) and 6(b) show examples of an SEM image and EBSD mapping of sample J observed along the normal direction, respectively. It was found from the SEM image that the Si layer was continuous. The EBSD measurement was carried out at intervals of 2 μm within an area of 200×200 μm$^2$. In Fig. 6(b), regions of (111)-oriented Si grains are colored blue, and regions of (001)-oriented Si grains are colored red. In the present study, (111)-oriented grains were defined as grains whose misorientation from the ideal (111) plane was less than 10°. Figure 6(b) reveals that approximately 94% of the film surface area had a preferential orientation of (111). The RMS roughness value of the poly-Si layer was relatively large, at 14.72 nm.

3.2 Formation and photoresponsivity of BaSi$_2$ film on AIC-Si/SiO$_2$

Figure 7(a) shows the $\theta$-2$\theta$ and 2$\theta$ XRD patterns from the samples after the growth
of a 300-nm-thick Ba$_2$Si film by MBE on the Si layers formed by the AIC process of sample J.

The diffraction peaks of the (211), (301) and (411) planes of Ba$_2$Si were observed instead of $a$-axis-oriented diffraction peaks which dominate in the Ba$_2$Si epitaxial films grown on single-crystalline Si(111) substrates [12]. We think that this can be attributed to the rough surface of the AIC-Si layers, as mentioned above. Epitaxial thickening by chemical vapor deposition utilizing the AIC poly-Si layers as seed crystals might lead to a flat surface of the poly-Si layers, thereby yielding $a$-axis-oriented high-quality Ba$_2$Si layers. Figure 7(b) shows the external quantum efficiency ($\eta$) versus photon energy measured at RT under various bias voltages. Light absorption produces electron-hole pairs that are separated by the electric field between the electrodes, leading to current flow in the external circuit as the photoexcited carriers drift before recombination. Photocurrents were observed for photon energies greater than 1.25 eV, and increased sharply with increasing photon energy to reach a maximum at approximately 1.60 eV. For comparison, the $\eta$ versus photon energy plot measured for the AIC-Si layers in sample J was inserted in Fig. 7(b). The $\eta$ value was more than two orders of magnitude smaller than that for the Ba$_2$Si sample. Thus, the contribution of photoexcited carriers originating from the AIC-Si layers to the measured photoresponse can be excluded. This is because the $\alpha$ value of Ba$_2$Si exceeds $10^5$ cm$^{-1}$ at around 1.60 eV [2,3], and therefore almost all the photons around 1.60 eV are absorbed within the 300-nm-thick Ba$_2$Si film. $\eta$ was found to reach a value as large as approximately 8% at a bias voltage of 5 V. This value
corresponds to that obtained in 900-nm-thick BaSi$_2$ epitaxial films on single-crystalline Si(111) substrates [19]. In this study, photoexcited carriers drifted in the lateral direction, and therefore the carriers likely encountered grain boundaries. With increasing drift velocity, the number of carriers that reached the electrodes before recombination increased, resulting in an increase in the external quantum efficiency with increasing bias voltage, as shown in Fig. 7(b).

In the case of a BaSi$_2$ $pn$ junction, an enhanced external quantum efficiency can be expected, because a much larger built-in electric field ($\sim 10^4$ V/cm) exists around the junction, and also the distance that photoexcited carriers must travel is much shorter ($\sim 1$ μm) than that in the present case (1.5 mm). The highest temperature used in this study was 600 °C, and that is the temperature when BaSi$_2$ films were grown by MBE. Thus, the whole process can be carried out for cheaper substrates than fused silica substrates in the near future.

4. Conclusions

We have prepared (111)-oriented Si layers on fused silica substrates by the AIC method. The dependence of the crystallinity on the thicknesses of the Si and Al layers, deposition order and deposition technique, and air-exposure time after Al deposition was studied. It was found that vacuum evaporation of Al and subsequent exposure to air significantly improved the crystallinity of AIC-Si layers. EBSD mapping revealed that approximately 94% of the AIC-Si surface area had a preferential (111) orientation.
300-nm-thick undoped-BaSi$_2$ films were grown by MBE on (111)-oriented Si layers produced on SiO$_2$ by the AIC method. Photoresponse spectra for photons with energies greater than 1.25 eV were clearly observed. The external quantum efficiency at 1.60 eV increased with the bias voltage applied between the electrodes, and reached a value of approximately 8% at 5 V.
References


Figure captions

Figure 1  \(\theta-2\theta\) and \(2\theta\) XRD patterns of samples A-E. The X-ray beam was incident at an angle of 2° in the \(2\theta\) XRD measurement. Sample preparation is summarized in Table 1. The Al layers were not etched for these measurements.

Figure 2  AFM images of samples B and E. In the case of sample B, the Al layer was etched before measurement.

Figure 3  \(\theta-2\theta\) and \(2\theta\) XRD patterns of samples F-J. \(\theta-2\theta\) and \(2\theta\) XRD patterns of samples A-E. The X-ray beam was incident at an angle of 2° in the \(2\theta\) XRD measurement. Sample preparation is summarized in Table 2. The Al layers were not etched for these measurements.

Figure 4  AFM images of samples B and J taken just after Al deposition by RF magnetron sputtering (a) and by vacuum evaporation (c), and after 50-h-exposure to air (b) and after 48-h-exposure to air (d), respectively.

Figure 5  Dependence of XRD peak intensity of Si(111) plane on exposure time to
air after Al deposition. The experimental conditions were the same as those for sample J except for the exposure time. The solid line is a guide only.

Figure 6 (a) SEM image and (b) EBSD mapping of the AIC-Si layer in sample J. observed along the normal direction. (111)-oriented grains were defined as grains whose misorientation from the ideal (111) plane was less than 10°.

Figure 7 (a) θ-2θ and 2θ XRD patterns of BaSi₂ on SiO₂ and (b) external quantum efficiency vs. photon energy for BaSi₂ layers measured at RT. The quantum efficiency for the AIC-Si layer (sample J) multiplied by 10 under the bias voltage of 2 V is inserted for comparison.