Realization of Crystalline BaSi\textsubscript{2} Thin Films by Vacuum Evaporation on (111)-oriented Si Layers Fabricated by Aluminum Induced Crystallization

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We have realized single phase crystalline BaSi\textsubscript{2} thin films on quartz substrate by vacuum evaporation for solar cell applications. This structure is achieved by introducing (111)-oriented poly-Si fabricated by aluminum induced crystallization as a supply layer prior to BaSi\textsubscript{2} deposition. Raman measurements showed five characteristic peaks corresponding to [Si\textsubscript{4}]\textsuperscript{4−} anions vibrations in BaSi\textsubscript{2} for all films deposited at 400°C and above. X-ray diffraction analysis showed that randomly-oriented orthorhombic phase of BaSi\textsubscript{2} is achieved with no trace of secondary phases. Also, the crystal quality is enhanced at higher substrate temperatures.

1. Introduction

Recently, BaSi\textsubscript{2} is receiving much attention as light absorbing material especially for solar cell applications. Compared to conventional Si, BaSi\textsubscript{2} has two major advantages. The bandgap (1.13-1.34 eV \cite{1,2}) matches with the solar spectrum, and it has very high absorption coefficient (3×10\textsuperscript{4} at 1.5 eV \cite{1}). This makes the fabrication of high efficiency solar cells with reduced thickness becomes conceivable. Furthermore, Ba and Si are abundant in earth crust which is advantageous for large scale mass production.

Epitaxial BaSi\textsubscript{2} layers with \textit{a}-axis orientation of (100) have been successfully grown on Si(111) by reactive deposition epitaxy followed by molecular beam epitaxy (MBE) \cite{3}, Si(111) is a suitable substrate for BaSi\textsubscript{2} epitaxial growth since the lattice mismatch of BaSi\textsubscript{2}[010]/Si[112] and BaSi\textsubscript{2}[001]/Si[110] is only 1.0\% and 0.1\%, respectively \cite{4}. The resulting undoped BaSi\textsubscript{2} epitaxial thin films have low electron concentration of 10\textsuperscript{16} cm\textsuperscript{-3} \cite{5} and long minority carrier lifetime for thin film solar cells \cite{6}.

Another successful method for producing BaSi\textsubscript{2} is by vacuum evaporation. Unlike MBE, fast deposition rate can be achieved by vacuum evaporation at pressure higher than that of MBE method. In our previous studies, we have confirmed that during evaporation of BaSi\textsubscript{2} source (lumps), the vapor content is inhomogeneous: the initial vapor is Ba-rich, while the latter is Si-rich. We found that high Si substrate temperatures (≥500°C) are required to promote solid state reaction of Ba-rich layer with Si substrate, which produces single-phase BaSi\textsubscript{2} films \cite{7,8}.

So far, we have attempted and succeeded in realizing single-phase crystalline BaSi\textsubscript{2} on glass substrates. Since the initial vapor produced from the BaSi\textsubscript{2} source is Ba-rich in composition, Si layers must be additionally supplied for the formation of stoichiometric BaSi\textsubscript{2}. In our previous study, we have shown that single-phase BaSi\textsubscript{2} with better crystalline quality is achieved on CaF\textsubscript{2} substrate by introducing amorphous Si (a-Si) as supply layers prior to BaSi\textsubscript{2} deposition. However, we found
defective parts on the bottom of BaSi$_2$ layers containing BaSi$_2$ microcrystals with Ar inclusion which come from Si deposition atmosphere.$^{[9]}$ In this study, instead of using a-Si as supply layers, we introduced poly-Si layers fabricated by aluminum induced crystallization (AIC). There are three considered merits of using AIC method. First, AIC allows us to fabricate large grained poly-Si layers.$^{[10]}$ which may eliminate the aforementioned defective problems caused by Ar content in a-Si layers. Second, since AIC proceeds under nearly equilibrium conditions, heavily doped p-type poly-Si by Al atoms can be expected$^{[11]}$, which might be utilized to realize p-type BaSi$_2$ films. And third, highly uniform (111)-oriented quasi-single crystal structure can be achieved on SiO$_2$ substrate by AIC.$^{[12]}$. By using (111)-oriented poly-Si templates, epitaxial growth of high quality $a$-axis oriented BaSi$_2$ is expected.

2. Experimental Methods
2.1 AIC-Si Growth
Sputtering method was used to deposit Al and Si on SiO$_2$ substrate. The deposition rate of Al and Si were measured to be 6.0 and 4.0 nm/min, respectively. The substrates were cleaned by standard RCA method followed by ultrasonic cleaning in distilled water. About 50 nm-thick Al were deposited on SiO$_2$ substrate. Prior to Si deposition, the process was stopped and Al layers were exposed into air to form native oxide layers. Then about 65 nm-thick Si were deposited on this layer. The resulting samples were then annealed in dry Ar ambient atmosphere while being observed by an optical microscope. The annealing temperature was varied at 475, 500, and 525 $^\circ$C, while the annealing time until completion was 12 h, 5 h, and 1 h for each respective temperature. During this process, layer exchange between a-Si and Al occurs which leads to the growth of poly-Si. To remove the unwanted Al layers, 5% HF etching followed by Secco etching were performed. The crystal orientation of the resulting AIC-Si samples is measured by electron backscattering diffraction (EBSD).

2.2 BaSi$_2$ Growth
Commercial BaSi$_2$ lumps (99% in purity, Kojundo Chemical Lab.) were used as source materials. This source was placed on a tungsten boat and was allowed to melt by resistive heating of tungsten boat inside vacuum chamber with pressure lower than 1.0 x 10$^{-5}$ mbar. The evaporated atoms were deposited on glass substrate with AIC-Si supply layers prepared earlier. Substrate temperatures were set at room temperature (RT), 400, 500, and 600 $^\circ$C. The evaporation time was kept at 1 min 40 seconds to exhaust BaSi$_2$ source while preventing further Si deposition due to reaction of BaSi$_2$ and tungsten boat during evaporation.$^{[8]}$. The structure of the grown samples were characterized by Raman spectroscopy (Tokyo Instruments Nanofinder) with Ar+ ion laser ($\lambda$ = 488 nm) and X-ray diffraction analysis (Bruker Discover D8) with Cu K$\alpha$ source radiation. Meanwhile the cross-section and surface imaging of the grown films were measured by scanning electron microscopy (SEM: JEOL JSM-7001FA). Finally the electrical properties was measured Hall measurement.

3. Results and Discussions
3.1 Crystal growth mechanism and crystal orientation of AIC-Si
Figure 1 shows the crystal growth profile of poly-Si on SiO$_2$ substrate during layer exchange of AIC process. During annealing process, a-Si layers diffused into Al layers through aluminum oxide barrier layers. When Si concentration in Al reaches saturation concentration, Si nuclei begin to grow$^{[13]}$. During the crystal growth process, two stages of growth can be distinguished. The first stage is called “nucleation stage” [Fig. 1(a-c)]. This stage is started when Si nucleus begin to form. During this
stage, new nuclei appear while the existing nucleus grow. This stage ends when new nucleus are no longer formed. After that, the crystal grains grow and expand two-dimensionally from their respective nucleus sites [44]. This stage is called “crystallization stage” [Fig. 1(d-f)]. During the first stage, nucleus density was found to be strongly dependent on annealing temperature. Nucleus density increases along with the increase of annealing temperature. From microscope imaging, nucleus density of about 0.5, 1.8, and $6.3 \times 10^4 \text{ cm}^{-2}$ are observed for annealing temperature of 475, 500 and 525 °C respectively [Fig. 1(a-c)]. The increase of nucleation density is probably caused by enhanced diffusion rate of Si by increased thermal energy, thus saturation concentration of Si can be achieved faster which leads to multiplication of nucleation sites.

Figure 2 shows the EBSD inversed pole figure diagrams of the grown AIC-Si. The blue color represents (111)-orientation of Si as shown in the color legend [Fig. 2(d)]. It can be shown that for AIC-Si grown at 475 °C, quasi-single crystal with (111)-preferred orientation is achieved [Fig. 2(a)]. However, orientations other than (111) appear at higher annealing temperatures [Fig. 2(b-c)]. The appearance of random orientations other than (111) is somehow related to the nucleus density. At higher temperature, due to enhanced diffusion rate of Si atoms into Al layers, saturation concentration of Si in Al is satisfied before Si atoms reached the interface between glass substrate and Al layers. Thus random nucleation may occur in the bulk of Al layers. Some has reported such non-interface
nucleation has (001) orientation $[12]$. The resulting AIC-Si grown at 475 °C are found to be $p$-type film with holes density ($p$) of $5.43 \times 10^{18}$ cm$^{-3}$.

3.2 Grown BaSi$_2$ films structural properties
BaSi$_2$ films were deposited on SiO$_2$ substrates with AIC-Si supply layers grown at 475 °C. Initially, about 0.15 gr of BaSi$_2$ source was used to deposit BaSi$_2$. After vacuum evaporation process, we found approximately 0.01 gr of source leftover product on tungsten boat. This product may come from reaction process between BaSi$_2$ and tungsten boat during evaporation as it is explained in our previous study $[8]$. Figures 3(a-c) show cross-sectional SEM images of BaSi$_2$ films grown on SiO$_2$ substrate with AIC-Si supply layers. Although the BaSi$_2$ source material was kept to be the same in amount, the thickness of the resulting films varies dependently to the substrate temperature. From the cross-sectional and surface images, about 657-nm-thick porous film with rough surface is observed for a substrate temperature of 400 °C [Fig. 3(c, f)], while dense structure with smooth surface is achieved at 500 and 600 °C, (b, e) and (a, d) respectively. The decrease of film thickness is probably because re-evaporation velocities of the deposited atoms increase with the substrate temperature $[7]$. We found no trace of defective BaSi$_2$ parts due to Ar inclusions as they were observed in our previous study $[9]$. We suspect that trapped Ar gas was released during crystallization of Si in AIC process.

Figure 4 shows Raman spectra of the grown BaSi$_2$ films. The films deposited at RT, 400, 500, and 600 °C exhibited five characteristic peaks in the range of 250-500 cm$^{-1}$. These peaks are attributed to vibration mode of [Si$_4$]$_4^-$ anions in BaSi$_2$ $[13]$. Meanwhile the film deposited at RT showed no trace of any peaks. These results indicate that BaSi$_2$ phase structure is achieved at substrate temperature starting from 400 °C and higher. It is interesting to note that the peaks intensity is increased with the

![Cross-section (a-c) and surface images (d-f) of the grown BaSi$_2$ on SiO$_2$ substrate with AIC-Si supply layers at 600, 500, and 400 °C, (a, d), (b, e), and (c, f) respectively. The films thickness decreases with the substrate temperature. Porous structure with rough surface of BaSi$_2$ film is formed at 400 °C (c, f), while dense structure with smooth surface is achieved at 500 and 600 °C, (b, e) and (a, d) respectively. The decrease of film thickness is probably because re-evaporation velocities of the deposited atoms increase with the substrate temperature.](image-url)
substrate temperature, indicating crystal quality enhancement at higher temperatures.

In order to confirm the phase and the crystal structure of the grown BaSi$_2$ films, XRD patterns of the films were taken (Fig. 5). The XRD peaks position of the films deposited at 400, 500 and 600 °C are found to be matched with the calculated $2\theta$-$\theta$ patterns of randomly oriented orthorhombic BaSi$_2$. No other peaks are found which confirms that the grown BaSi$_2$ films are single-phase. The peaks exhibited by the films deposited at 500 and 600 °C are markedly strong. The resulting BaSi$_2$ grown at these temperatures are therefore randomly-oriented polycrystals. On the other hand, weak peaks are shown by the films deposited at 400 °C. This may suggest that the resulting crystal has low

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**Fig. 4.** Raman spectra of the grown BaSi$_2$ on SiO$_2$ substrate with AIC-Si supply layers at RT, 400, 500, and 600 °C. Raman peaks intensity is increased with substrate temperature.

**Fig. 5.** XRD patterns of the grown BaSi$_2$ on SiO$_2$ substrate with AIC-Si supply layers at RT, 400, 500, and 600 °C. Weak XRD signals are observed for the films grown at 400 °C, while strong signals are observed at 500 and 600 °C.
crystallinity. It is interesting to note that instead of $a$-axis orientation, randomly-oriented $\text{BaSi}_2$ is achieved by vacuum evaporation in this study. This is probably because deposition rate by vacuum evaporation is so much faster than that of MBE method so that epitaxial growth of $\text{BaSi}_2$ cannot be achieved under the deposition condition used in this study. We suspect that the control of the vapor composition during film growth may play an important role in realizing epitaxial growth of $\text{BaSi}_2$ by vacuum evaporation. Instead of $p$-type, we obtained $n$-type $\text{BaSi}_2$ film which is out of our expectation. The measured electron density ($n$) and mobility ($\mu$) of the grown $\text{BaSi}_2$ at 500 °C was $1.54 \times 10^{19}$ cm$^{-3}$ and 1.68 cm$^2$/V s respectively. There are some possibilities that might cause this phenomena. The first is that Al dopant concentration might be insufficient to effectively dope $\text{BaSi}_2$ film. Also due to high ionization energy of Al dopants (69 meV) \cite{16} it is possible that only some fraction of Al dopants are activated. Furthermore, Al dopants have tendency to diffuse out of $\text{BaSi}_2$ and forming segregations at $\text{BaSi}_2$ surface or at the interface between $\text{BaSi}_2$ film and $\text{SiO}_2$ substrate due to high substrate temperature during evaporation process \cite{17}.  

4. Conclusion
Large grained quasi-single crystal Si with (111) orientation was successfully grown by AIC-method on $\text{SiO}_2$ substrate. This layer was employed as a supply layer prior to $\text{BaSi}_2$ deposition. Single-phase polycrystalline $\text{BaSi}_2$ were successfully fabricated by vacuum evaporation on this supply layer at substrate temperature of 400, 500, and 600 °C. Instead of $a$-axis orientation, $\text{BaSi}_2$ films with random orientations were achieved. At low substrate temperature ($\leq$400 °C), weak XRD signals may suggest low crystallinity of the resulting film. On the other hand, strong XRD peaks are observed for the films grown at 500 and 600 °C which indicates crystal quality enhancement at high substrate temperatures. Instead of $p$-type film, $n$-type $\text{BaSi}_2$ film was obtained. This might be due to insufficient Al dopant concentration, partial ionization of Al dopants, and the formation of Al segregations.

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References