Large photoresponsivity in semiconducting $BaSi_2$ epitaxial films grown on Si(001) substrates by molecular beam epitaxy

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Approximately 900- and 400-nm-thick $BaSi_2$ epitaxial films were grown on Si(111) and Si(001) substrates, respectively, by molecular beam epitaxy, and their photoresponse properties were compared at room temperature. When the bias voltage V_{bias} applied between the 1.5-mm-spacing stripe-shaped electrodes on the $BaSi_2$ surfaces increased, photocurrents were clearly observed for photon energies greater than the band gap for both samples. However, the photoresponsivity for $BaSi_2$ on Si(001) was more than 8 times larger than that for $BaSi_2$ on Si(111); reaching approximately 50 and 5 mA/W at 1.6 eV, respectively, when V_{bias} was 1.0 V. This is attributed to the difference in the grain size of $BaSi_2$ films confirmed by plan-view transmission electron microscopy.

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1. Introduction

It is important for solar cell materials to have a large absorption coefficient and a suitable band gap that matches the solar spectrum to yield high conversion efficiency. Among such materials, we have focused on semiconducting orthorhombic $BaSi_2$. The band gap of $BaSi_2$ is approximately 1.3 eV and can be increased up to 1.4 eV in $Ba_{1-x}Sr_xSi_2$ [1,2], which matches the ideal solar spectrum much better than crystalline Si. In addition, $BaSi_2$ has a very large absorption coefficient α of approximately 3×10^4 cm^{-1} at 1.5 eV [2]. A large value of α and expansion of the band gap in $Ba_{1-x}Sr_xSi_2$ were theoretically expected [3,4]. $BaSi_2$ can be grown epitaxially on a Si(111) substrate with the orientation alignment of $BaSi_2$(100)//Si(111), with a small lattice mismatch of 1.0% for $BaSi_2$[010]//Si[112] [5]. Therefore, lots of studies have been done on $BaSi_2$ epitaxial films grown on Si(111) by molecular beam epitaxy (MBE). Recently, we have achieved large photoresponsivity in undoped *n*-type $BaSi_2$ epitaxial layers on Si(111) and polycrystalline $BaSi_2$ layers on (111)-oriented polycrystalline Si layers on SiO_2 [6-8]. With respect to the lattice mismatch, we have considered that the (111) facet of a Si substrate is best for $BaSi_2$ growth, although the grain size of $BaSi_2$ is as small as approximately 0.2 μm [9]. This is because of three epitaxial variants, due to the sixfold symmetry of Si(111) [10], rotating around each other by 120° in the surface normal. Many grain boundaries and other defects in a film would deteriorate the optical and electrical properties. Thus, it is important to increase the grain size of $BaSi_2$ films. Note that *a*-axis oriented $BaSi_2$ was surprisingly grown on the Si(001) substrate, despite the large lattice mismatch of 0.1% for $BaSi_2$[001]//Si[110] and 12.5% for $BaSi_2$[010]//Si[110] [5]. Very recently, we found that the grain size of *a*-axis-oriented $BaSi_2$ epitaxial layers on Si(001) is more than 1 μm, much larger than that on Si(111) [11]. However, we have not yet measured photoresponse properties of $BaSi_2$ epitaxial films on Si(001). In this paper, we aimed to compare the photoresponsivity of $BaSi_2$ grown on Si(001) with that on Si(001), already reported in Ref. [7].

2. Experimental

An ion-pumped MBE system equipped with standard Knudsen cells for Ba and Sb, and an electron-beam evaporation source for Si was used. After cleaning Czochralski n-Si(111) (ρ=0.015 Ω·cm) and n-Si(001) (ρ=0.07 Ω·cm) substrates at 850 °C for 30 min in ultrahigh vacuum, approximately 850- and 350-nm-thick undoped *n*-$BaSi_2$ epitaxial films were grown on Si(111) and Si(001) substrates, respectively, by reactive deposition epitaxy (RDE; Ba deposition on hot Si) for $BaSi_2$ template layers, and subsequent MBE (codeposition of Ba and Si on Si) to form thick $BaSi_2$ films. Details of the growth procedure have been previously described [7,11]. Finally, approximately 50-nm-thick Sb-doped n^+-$BaSi_2$ (~10^{20} cm^{-3}) layer was formed for ohmic contacts [12]. For photoresponse measurements, Cr and Au were evaporated on the surface to form 1.5-mm-spacing stripe-shaped electrodes. The photocurrent flowing in the lateral direction between the electrodes was evaluated by a lock-in technique using a 150 W Xenon lamp (5 mW/cm^2 at 470 nm) with a 25-cm focal-length single monochromator (Bunkoukeiki SM-1700A). The light intensity was calibrated by a pyroelectric sensor (MELLES GRIOT 13PEM001/J). The crystalline quality of the grown films was characterized by reflection high-energy electron diffraction (RHEED), X-ray diffraction (XRD), and transmission electron microscopy (TEM).

3. Results and discussion

Figure 1 show the RHEED patterns of $BaSi_2$ films after (a) RDE at 550 °C and (a’) MBE at 600 °C on Si(111), and after (b) RDE at 530 °C and (b’) MBE at 580 °C on Si(001) substrates. The RHEED patters were observed along the Si[11-2] and Si[110], respectively. We can see clear streaky RHEED patterns for $BaSi_2$ films on Si(111), which is typical for *a*-axis-oriented $BaSi_2$ epitaxial films [13]. On the other hand, two clear sets of streaky patterns with different spacings are seen for $BaSi_2$ on Si(001), in Figs. 1(b) and 1(b'). The ratio of wide streaky spacing to narrow spacing is approximately 1.7, which is explained by the ratio of $1/b$ to $1/c$. Taking into account that the electron beam was incident along the Si[110] azimuth, these two streaky patterns with different spacings indicate the existence of two epitaxial variants rotating 90° to each other in the surface normal; $BaSi_2$(100)//Si(001) with $BaSi_2$[010]//Si[110] and $BaSi_2$[001]//Si[110] [11].

Figures 2(a) and 2(b) present the θ-2θ XRD patterns of $BaSi_2$ films on Si(111) and Si(001) substrates, respectively. The diffraction peaks at $2\theta = 20^o$, 41^o, 63^o correspond to $BaSi_2$(200), (400), and (600) planes, respectively, indicating that highly *a*-axis-oriented $BaSi_2$ films were grown.

Figures 3(a) and 3(b) shows the plan-view bright-field (BF) TEM images of $BaSi_2$ films on (a) Si(111) and (b) Si(001) substrates. The incident electron beam was almost parallel to the $BaSi_2$[100] zone axis, but was slightly tilted for the grain boundaries (GBs) to be seen clearly. We can easily see that the grain size of the $BaSi_2$ film on Si(111) is approximately 0.2 μm. In contrast, theg grains of more than 1 μm in diameters exist in the $BaSi_2$ film on Si(001) in Fig. 3(b). We speculate that the large grain of $BaSi_2$ on Si(001) is partly due to the reduced number of epitaxial variants from three for $BaSi_2$ on Si(111) to two for $BaSi_2$ on Si(001). However, the difference in grain size is significantly larger than expected. Thus, further studies are required to clarify the mechanism that explains this difference.

Figures 4(a) and 4(b) show the photoresponse spectra measured at RT under various bias voltages applied between the 1.5-mm-spacing stripe-shaped Au/Cr electrodes on the surface of $BaSi_2$ films on (a) Si(111) and (b) Si(001) substrates. In both samples, photocurrents increased sharply with increasing bias voltages V_{bias} for photon energies greater than the band gap. However, the magnitude of photoresponsivity differed significantly between them. The photoresponsivity reached 13 mA/W at 1.6 eV for $BaSi_2$ on Si(111) when V_{bias} was 2.5 V on Si(111), while it marked approximately 100 mA/W for $BaSi_2$ on Si(001). This difference is attributed to the difference in the grain size of $BaSi_2$ films. It should be noted that in the photoresponse spectra, peaks become pronounced at 1.46 eV. This is due to the non-linear property of the photocurrent caused by the intense line-shaped spectrum of the Xenon light at this photon energy. On the basis of these results, we concluded that the further improvement of photoresponsivity in $BaSi_2$ epitaxial films is expected with much larger grains. In this sense, a Si(001) face is more preferable for $BaSi_2$ than a Si(111) surface.

4. **Summary**

Approximately 900- and 400-nm-thick $BaSi_2$ epitaxial films were grown on Si(111) and Si(001) substrates, respectively, by MBE. Plan-view BF TEM images revealed that the grain size of $BaSi_2$ on Si(001) was more than 1 μm, while that on Si(111) was approximately 0.2 μm. When the bias voltage V_{bias} was 2.5 V, the photoresponsivity reached 100 mA/W for $BaSi_2$ on Si(001) at 1.6 eV. On the other hand, it was only 13 mA/W for $BaSi_2$ on Si(111).

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Fig. 1 RHEED patterns of $BaSi_2$ films after (a) RDE at 550 °C and (a') MBE at 600 °C on Si(111), and after (b) RDE at 530 °C and (b') MBE at 580 °C on Si(001) substrates, observed along Si [110] and Si[11-2], respectively. The arrows show the existence of two sets of streaky patterns with different spacings for $BaSi_2$ on Si(001).

Fig. 2 θ-2θ XRD patterns of $BaSi_2$ films on (a) Si(111) and (b) Si(001) substrates. The forbidden diffraction peaks caused by the Si substrates are indicated by asterisks.

Fig. 3 Plan-view BF TEM images of $BaSi_2$ films on (a) Si(111) and (b) Si(001) substrates. The incident electron beam was almost parallel to the $BaSi_2$[100] zone axis, but was slightly tilted for the GBs to be seen clearly.

Fig. 4 Photoresponse spectra measured at RT under various bias voltages applied between the 1.5-mm-spacing stripe-shaped Au/Cr electrodes on the surface of $BaSi_2$ films on (a) Si(111) and (b) Si(001) substrate

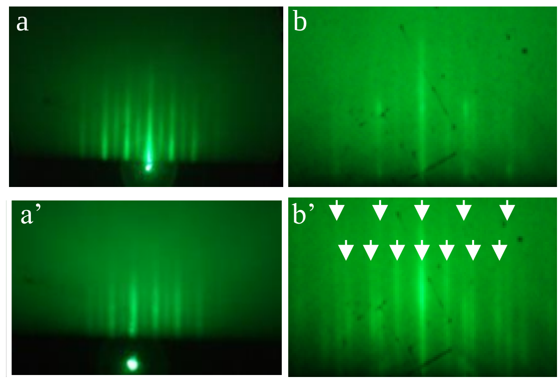
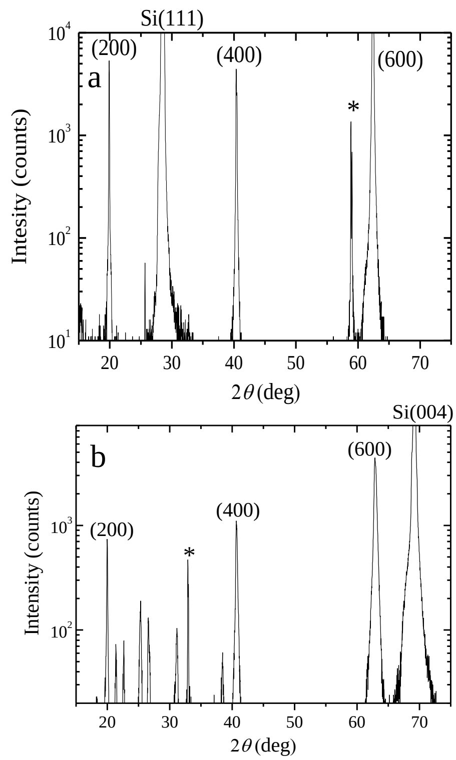


Fig. 1



Si(111)
(200)
(400)
(600)
a
*
Intesity (counts)
2θ (deg)
Si(004)
b
(600)
(200)
*
(400)
Intensity (counts)
2θ (deg)

Fig. 2

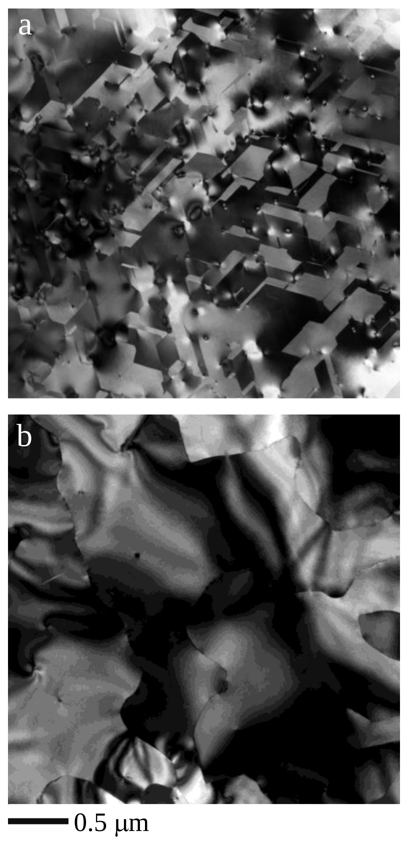
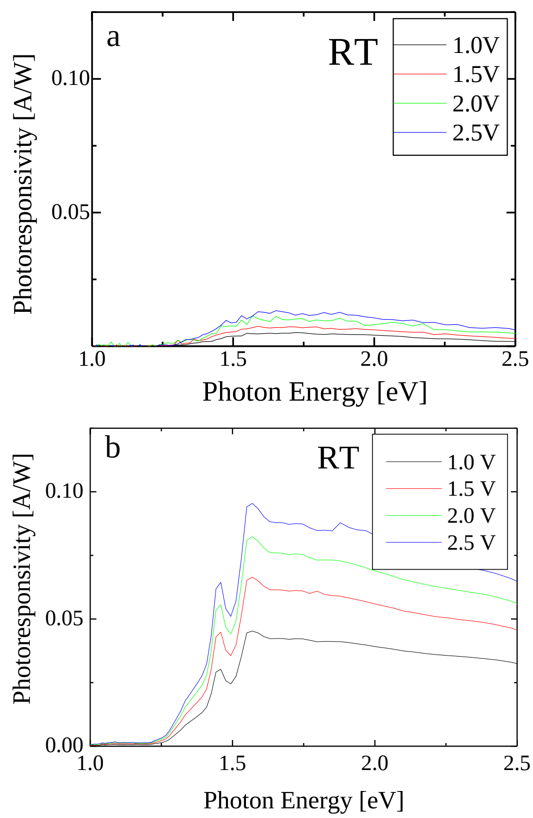


Fig. 3



a
RT
1.0V
1.5V
2.0V
2.5V
Photoresponsivity [A/W]
0.10
0.05
1.0
1.5
2.0
2.5
Photon Energy [eV]
b
RT
1.0 V
1.5 V
2.0 V
2.5 V
Photoresponsivity [A/W]
0.10
0.05
0.00
1.0
1.5
2.0
2.5
Photon Energy [eV]

Fig. 4