Growth and characterization of group-III impurity-doped semiconducting $BaSi_2$ films grown by molecular beam epitaxy

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Ga- or In-doped $BaSi_2$ films were grown on Si(111) by molecular beam epitaxy (MBE). The Ga-doped $BaSi_2$ showed *n*-type conductivity. The electron concentration and resistivity of the Ga-doped $BaSi_2$ depended on the Ga temperature; however, the electron concentration and resistivity could not be controlled properly. In contrast, the In-doped $BaSi_2$ showed *p*-type conductivity and its hole concentration was controlled in the range between 10^{16} and 10^{17} cm^{-3} at RT.

Keywords: $BaSi_2$, molecular beam epitaxy

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1. Introduction

Today, single crystal and polycrystalline Si predominate in solar cell materials. However, the band gap, E_g, of Si is as small as 1.1 eV at room temperature (RT). This value is approximately 0.3 eV smaller than the ideal band gap (~1.4 eV) for solar cells, resulting in low photoelectric conversion efficiency [1]. In addition, at least 200-μm-thick Si is required to produce crystalline Si solar cells due to its small optical absorption coefficient α. Therefore, new Si-based materials are required for high-efficiency thin-film solar cells. Semiconducting $BaSi_2$ is considered to be promising as such a material. $BaSi_2$ is an indirect band-gap semiconductor [2], stable at RT and atmospheric pressure [3], and is a better match for the Si(111) face than Si(001) with a lattice mismatch of less than 1.5% [4]. We have developed an epitaxial growth technique for $BaSi_2$ and $Ba_{1-x}Sr_xSi_2$ on Si(111) substrates by molecular beam epitaxy (MBE) using a $BaSi_2$ template [5-7]. The E_g value of $BaSi_2$ is approximately 1.3 eV [2, 8-10], and α for this material reaches 10^5 cm^{-1} at 1.5 eV [2], which is approximately two orders of magnitude higher than that of Si. Furthermore, the E_g value can be increased up to approximately 1.4 eV, matching the solar spectrum, by replacing half of the Ba atoms in $BaSi_2$ with isoelectric Sr atoms [11]. Thus, $BaSi_2$ is considered to be a good candidate for high-efficiency thin-film solar cells. A *p-n* junction is a basic structure of solar cells, wherein photo-excited electrons and holes are separated by the electric field around the *p-n* junction. Therefore, we need to be able to control the conductivity of $BaSi_2$.

However, there have been no reports thus far on impurity doping into $BaSi_2$ for controlling its conductivity.

The purpose of this study is to form group-III impurity-doped $BaSi_2$ films by MBE and to evaluate their electrical properties. We chose Ga and In as the group-III elements for doping.

2. Experimental

An ion-pumped MBE system equipped with standard Knudsen cells for Ba, Ga and In, and an electron-beam evaporation source for Si was used for the epitaxial growth. The deposition rates of these materials were controlled using a quartz crystal monitor. For electrical measurements, high-resistivity floating-zone *p*-Si(111) (ρ=1000-6000 Ω·cm) substrates were used. After cleaning the Si(111) substrate at 850ºC for 30 min in ultrahigh vacuum (UHV), a well-developed 7×7 reflection high-energy electron diffraction (RHEED) pattern was confirmed. RHEED patterns were observed along the [1-10] azimuth of the Si(111) substrate.

MBE growth of Ga- or In-doped $BaSi_2$ films was carried out as follows. First, a 20-nm-thick $BaSi_2$ epitaxial film was grown on Si(111) at 550ºC by reactive deposition epitaxy (RDE) and used as a template for $BaSi_2$ overlayers. Next, Ba, Ga (or In) and Si were co-evaporated on the $BaSi_2$ template at 600ºC to form Ga- (or In-) doped $BaSi_2$ by MBE. The thickness of the grown layers including the template was approximately 250 nm. Details of MBE growth of $BaSi_2$ have already been reported in our previous papers [5-7]. The ratio of Ga vapor pressure to that of Ba (Ga/Ba ratio) was varied from approximately 1/1000 to 1/100 by changing the temperature of the Ga, T_{Ga}. The ratio of In vapor pressure to that of Ba (In/Ba ratio) was varied from approximately 1/1000 to 1/10 by changing the temperature of In, T_{In}.

The crystal quality of the grown layers was characterized by X-ray diffraction (XRD) measurements. The electrical properties were characterized by Hall measurements using the van der Pauw method. The applied magnetic field was 0.2 T normal to the sample surface.

3. Results and discussion

3.1 Ga-doped $BaSi_2$

Figure 1 shows the $\theta-2\theta$ XRD patterns for undoped $BaSi_2$ and Ga-doped $BaSi_2$. Diffraction peaks of [100]-oriented $BaSi_2$ are observed for the undoped $BaSi_2$, showing that $BaSi_2$ was grown epitaxially. However, by increasing the Ga temperature, the [100]-oriented peaks exhibit a decrease in intensity, and several diffraction peaks other than those of [100]-oriented $BaSi_2$ begin to appear. These results show that Ga doping deteriorated the crystallinity of the grown layers, and polycrystalline $BaSi_2$ was formed.

Undoped $BaSi_2$ showed *n*-type conductivity. However, it was often difficult to obtain steady Hall voltages on the undoped $BaSi_2$ at RT because it was often difficult to make ohmic contacts due to its high resistivity. On the other hand, ohmic contacts were easily formed on Ga-doped $BaSi_2$. All the Ga-doped $BaSi_2$ specimens showed *n*-type conductivity in this work. This indicates that some of the Ba atoms in the $BaSi_2$ lattice structure were replaced by Ga atoms, thereby generating electrons. Figure 2 shows the T_{Ga} dependence of resistivity ρ and electron concentration n. For Ga-doped $BaSi_2$ prepared with $T_{Ga} > 800$ºC, the values of n and ρ are on the order of 10^{20} cm^{-3} and several mΩ·cm, respectively. They do not show distinct dependence on T_{Ga}. In contrast, the n and ρ values changed drastically for the Ga-doped $BaSi_2$ formed with $T_{Ga} < 800$ºC. They are on the order of 10^{15} cm^{-3} and several Ω·cm, respectively, and also do not show distinct dependence on T_{Ga}. The Ga/Ba ratio of these samples was approximately 1/1000. Thus, we suppose that most of the doped Ga atoms were not activated. The origin of this abrupt step-like change is not clear at present and is under investigation. We have to note that the values of n and ρ, obtained for Ga-doped $BaSi_2$ formed with $T_{Ga} < 800$ºC, include some amount of errors. Assuming that a built-in potential at the *n*-$BaSi_2$/*p*-Si interface is 1 V and a dielectric constant of $BaSi_2$ is 12, a depletion width in the *n*-$BaSi_2$ is estimated to be approximately 0.1 μm when the n values come to the order of $10^{15}cm^{-3}$. This value of 0.1 μm is comparable to the grown thickness of the *n*-$BaSi_2$. In order to obtain reliable n and ρ values, at least 1-μm-thick *n*-$BaSi_2$ is required.

Figure 3 shows the temperature dependence of the electron concentration n in Ga-doped $BaSi_2$ prepared with T_{Ga}=700ºC. The electron concentration decreased with decreasing temperature. This temperature dependence is typical for *n*-type semiconductors. The activation energy E_D was derived to be approximately 0.12 eV, assuming that the electron concentration obeys the following equation:

$$n(T) \propto \exp(-\frac{E_D}{2kT}),$$

where k is the Boltzmann constant and T is the absolute temperature. The electron mobility μ is approximately 300 $cm^2/V\cdot s$ at RT, and reaches a maximum value of 1800 $cm^2/V\cdot s$ at 200 K.

Figure 4 shows the temperature dependence of the resistivity ρ for the two samples, that is, the Ga-doped $BaSi_2$ prepared with T_{Ga} of 700ºC and 800ºC. For the sample prepared with T_{Ga}=700ºC, ρ increases with decreasing temperature. This temperature dependence is typical in semiconductors. In contrast, ρ is approximately 0.002 Ω·cm at RT and decreases slightly with decreasing temperature for the sample prepared with T_{Ga}=800ºC, suggesting that this Ga-doped $BaSi_2$ is almost degenerated. On the basis of these results, it can be stated that it is difficult to control the electron concentration in $BaSi_2$ by doping Ga. Thus, we conclude that Ga is not suitable as an *n*-type dopant for $BaSi_2$.

3.2 In-doped $BaSi_2$

Next, we selected In as another group-III impurity atom and attempted to use it to dope $BaSi_2$. Figure 5 shows the θ−2θ XRD patterns for undoped $BaSi_2$ and In-doped $BaSi_2$. In contrast to the results obtained for Ga-doped $BaSi_2$, the diffraction peaks of [100]-oriented $BaSi_2$ are dominant over the whole range of the In/Ba ratios in this work, although weak diffraction of the (310) plane begins to appear for samples formed with $T_{\mathrm{In}} > 700$ºC.

Hall measurements were performed on the In-doped $BaSi_2$. All the In-doped $BaSi_2$ showed *p*-type conductivity. This indicates that some of the Si atoms in the $BaSi_2$ lattice structure were replaced by In atoms thereby generating holes. Figure 6 shows the T_{In} dependence of the hole concentration p measured at RT. The different data points indicate different measurements. The p value tends to increase with increasing T_{In} in the range of $550^\circ \leq T_{\mathrm{In}} \leq 650$ºC, meaning that epitaxial growth of *p*-type $BaSi_2$ was realized for the first time. At higher T_{In}, the p value almost saturates or scatters. We therefore assume that most of the In atoms doped in $BaSi_2$ were not activated in the heavily In-doped $BaSi_2$. Further studies are necessary in order to investigate whether the hole concentration can be controlled to within several orders of magnitude in $BaSi_2$ by doping In.

4. Conclusion

Ga- or In-doped $BaSi_2$ films were grown on Si(111) by MBE, and their electrical properties were investigated. Ga-doped $BaSi_2$ shows *n*-type conductivity. However, with increasing concentration of Ga atoms doped in $BaSi_2$, the crystalline quality of the films deteriorated. The electron density was on the order of 10^{15} cm^{-3} or 10^{20} cm^{-3}, and thus was not controlled properly by doping Ga. On the other hand, In-doped $BaSi_2$ unexpectedly showed *p*-type conductivity. The hole concentration was controlled in the range between 10^{16} and 10^{17} cm^{-3} at RT.

Acknowledgements

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Figure captions

Figure 1 $\theta-2\theta$ XRD patterns for undoped $BaSi_2$ and Ga-doped $BaSi_2$. The Ga temperature was varied from 700 to 850ºC.

Figure 2 T_{Ga} dependence of resistivity ρ and electron concentration n in Ga-doped $BaSi_2$ measured at RT.

Figure 3 Temperature dependence of electron concentration n in Ga-doped $BaSi_2$ prepared at T_{Ga}=700ºC.

Figure 4 Temperature dependence of resistivity ρ of Ga-doped $BaSi_2$ formed at T_{Ga}=700 and 800ºC.

Figure 5 $\theta-2\theta$ XRD patterns for undoped $BaSi_2$ and In-doped $BaSi_2$. T_{In} was varied from 550 to 750ºC.

Figure 6 Dependence of hole concentration p in In-doped $BaSi_2$ on T_{In} measured at RT.

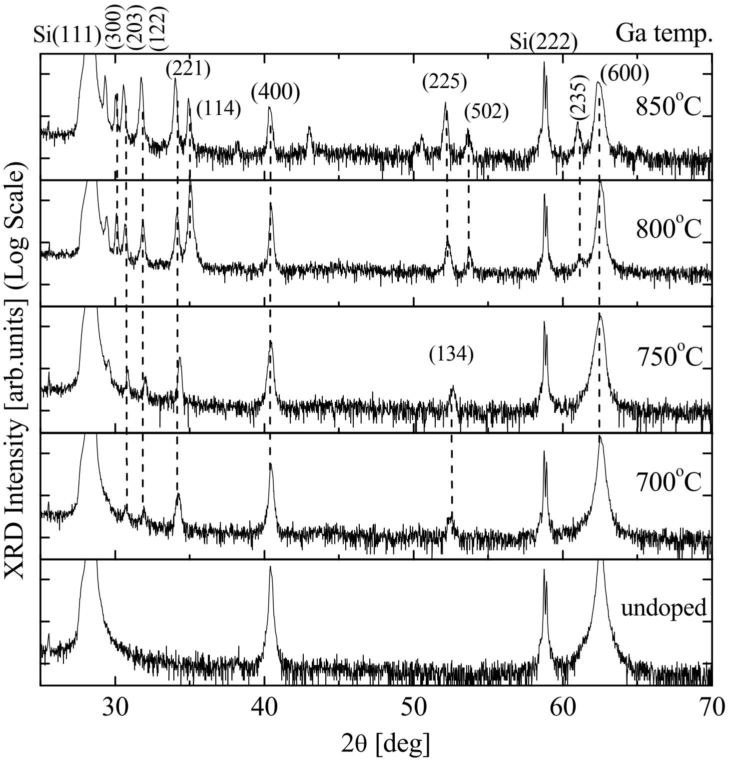

Figure 1 Kobayashi *et al.*

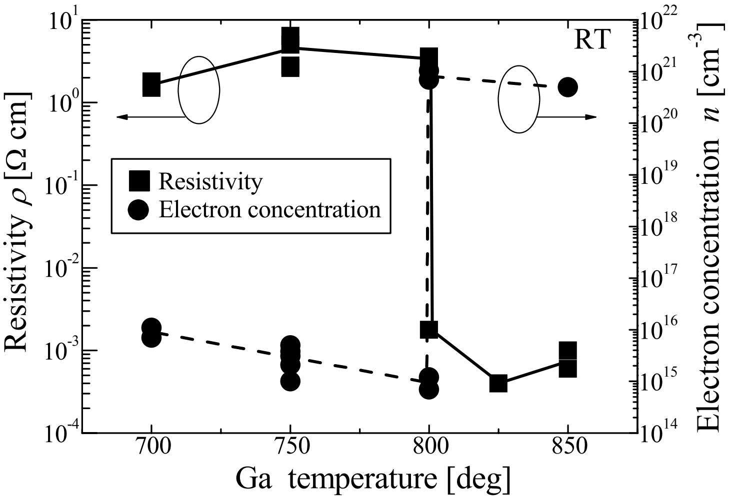

Figure 2 Kobayashi *et al.*

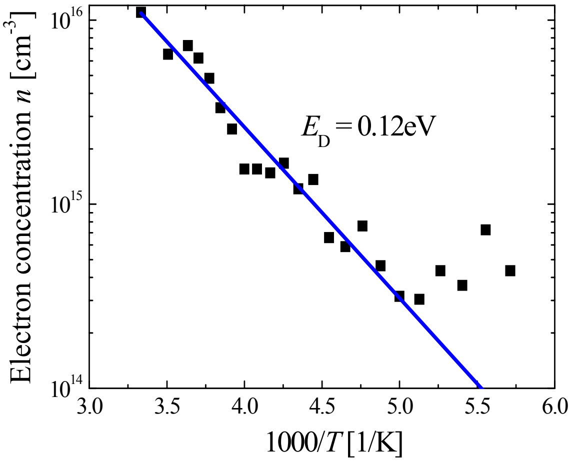

Figure 3 Kobayashi *et al.*

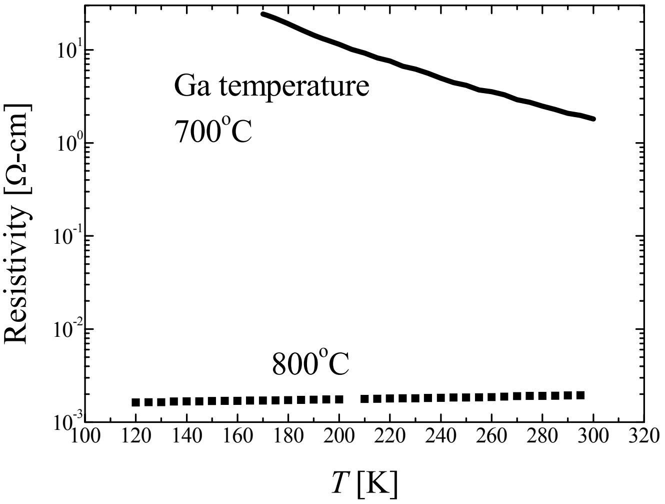

Figure 4   Kobayashi *et al.*

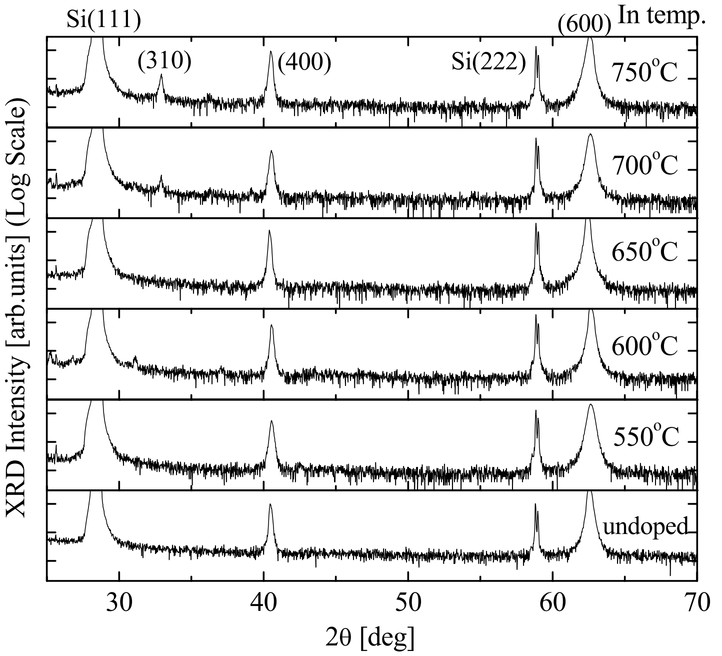

Figure 5 Kobayashi *et al.*

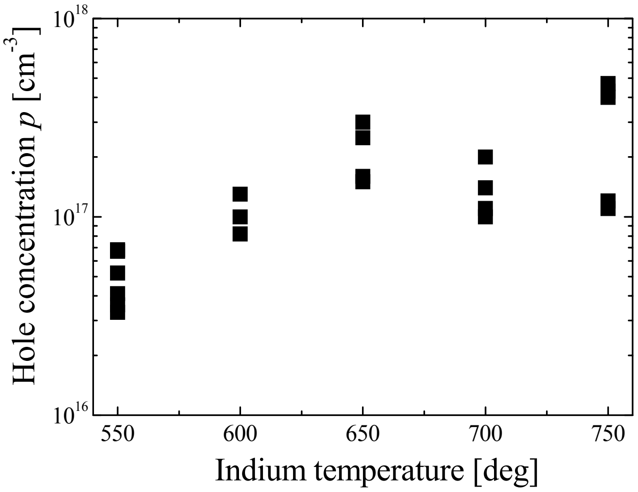

Figure 6   Kobayashi *et al.*