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In-situ heavily $p$-type doping of over $10^{20}$ cm$^{-3}$ in semiconducting BaSi$_2$ thin films for solar cells applications

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B-doped $p$-BaSi$_2$ layer growth by molecular beam epitaxy and the influence of rapid thermal annealing (RTA) on hole concentrations were presented. The hole concentration was controlled in the range between $10^{17}$ and $10^{20}$ cm$^{-3}$ at room temperature by changing the temperature of the B Knudsen cell crucible. The acceptor level of the B atoms was estimated to be approximately 23 meV. High hole concentrations exceeding $1 	imes 10^{20}$ cm$^{-3}$ were achieved via dopant activation using RTA at 800°C in Ar. The activation efficiency was increased up to 10%.

Materials for low cost, eco-friendly, and high efficiency solar cell applications have been of great importance. Among such materials, we have focused much attention on semiconducting BaSi$_2$. BaSi$_2$ has a simple orthorhombic structure and is considered a Zintl phase. It has an indirect band gap of approximately 1.3 eV, matching the solar spectrum. In addition, BaSi$_2$ has a large absorption coefficient of $3 \times 10^5$ cm$^{-1}$ at 1.5 eV, much larger than crystalline Si. Recent reports on high photoresponsivity and large internal quantum efficiencies exceeding 70% have spurred interest in this material. The remaining process was the formation of $p$-type BaSi$_2$ on the undoped $n$-type BaSi$_2$ layer ($\eta = 5 \times 10^{15}$ cm$^{-3}$) to complete the BaSi$_2$ pn junction diode. However, very little work has been done on the formation of impurity-doped BaSi$_2$ up to now. According to Imai and Watanabe, substitution of Si in the BaSi$_2$ lattice is more favorable than substitution of Ba from the energetic point of view. In line with this theoretical expectation, Sb-doped BaSi$_2$ exhibits $n$-type conductivity, while In- and Al-, and Ag-doped BaSi$_2$ exhibit $p$-type conductivity. The electron concentration of Sb-doped BaSi$_2$ was controlled in the range between $10^{17}$ and $10^{20}$ cm$^{-3}$ at room temperature (RT) by changing the temperature of the Sb Knudsen cell crucible. In contrast, the hole concentration was limited up to $3 \times 4 \times 10^{17}$ cm$^{-3}$ at RT in In-, Al-, and Ag-doped BaSi$_2$ layers. It is therefore highly required to find impurity atoms, with which heavily $p$-type doping is accomplished in BaSi$_2$. In this letter, we report the highest hole concentrations of over $10^{20}$ cm$^{-3}$ ever achieved for BaSi$_2$, by adopting B atoms as an impurity.

An ion-pumped molecular beam epitaxy (MBE) system equipped with standard Knudsen cells for Ba and B sources and an electron-beam evaporation source for Si was used for the growth of B-doped BaSi$_2$ films. Details of the growth procedures for impurity-doped BaSi$_2$ films are provided previously. Briefly, a 10-nm-thick BaSi$_2$ epitaxial film was first grown by reactive deposition epitaxy on floating-zone (FZ) n-Si(111) substrates ($\rho > 1000 \Omega$ cm) at substrate temperature, $T_s$, of 510°C, and then it was used as a template layer for BaSi$_2$ overlayers. Next, Ba, Si, and B were co-evaporated on the BaSi$_2$ template at $T_s = 600$ (samples A-E) or 650°C (sample G) to form approximately 240-nm-thick $a$-axis-oriented B-doped BaSi$_2$ epitaxial films by MBE. The temperature of B crucible, $T_B$, was varied from 1350 to 1575°C. The sample preparation methods used are summarized in Table I. After the MBE growth, rapid thermal annealing (RTA) was performed for several samples under Ar at 800°C for 0.5, 1, and 2 min for electrical activation of B atoms. The heating rate was 40°C/s. The electrical properties were characterized by Hall measurements using the van der Pauw method. The applied magnetic field was 0.7 T, normal to the sample surface. Depth profiles of B atoms in B-doped BaSi$_2$ films were characterized by secondary ion mass spectroscopy (SIMS) using O$_2$ ions.

Figure 1 shows the SIMS profiles of B atoms in samples A, C, and E. SIMS measurements revealed that the doped B atoms are distributed uniformly within the BaSi$_2$ layers. Their average B concentration, $N_B$, was approximately $3 \times 10^{20}$, $2 \times 10^{21}$, and $1 \times 10^{22}$ cm$^{-3}$ for samples A, C, and E, respectively. The B concentrations in the SIMS profiles were corrected using reference samples, where controlled number of B atoms was doped in the BaSi$_2$ films by ion implantations. The obtained B concentrations are explained relatively well by the difference in vapor pressure of B. The $N_B$ value in sample E was larger than that in sample G.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_s$ (°C)</th>
<th>$T_B$ (°C)</th>
<th>$p$ (cm$^{-3}$)</th>
<th>$\mu_p$ (cm$^2$/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>600</td>
<td>1350</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>B</td>
<td>600</td>
<td>1400</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>C</td>
<td>600</td>
<td>1450</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>D</td>
<td>600</td>
<td>1500</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>E</td>
<td>600</td>
<td>1550</td>
<td>$1.0 \times 10^{19}$</td>
<td>6.3</td>
</tr>
<tr>
<td>F</td>
<td>600</td>
<td>1575</td>
<td>$2.5 \times 10^{18}$</td>
<td>8.3</td>
</tr>
<tr>
<td>G</td>
<td>650</td>
<td>1450</td>
<td>$6.5 \times 10^{19}$</td>
<td>0.8</td>
</tr>
</tbody>
</table>

aEmail: suemasu@bk.tsukuba.ac.jp
sample C by 6–7 times. This is reasonable to think that the vapor pressure of B at 1550 °C is approximately 7 times larger than that at 1450 °C.  

B-doped as-grown BaSi2 showed p-type conductivity for samples E–G. For the other as-grown samples, however, it was difficult to obtain reliable carrier concentrations and mobilities due to difficulties in forming ohmic contacts on the surface. As described later, the RTA treatment enabled us to measure them for all the samples. Figure 2(a) shows the temperature dependence of hole concentrations in sample E. The hole concentration reached $1.0 \times 10^{19}$ cm$^{-3}$ at RT and decreased with decreasing temperatures. The acceptor level, $E_A$, calculated using Eq. (1) was 23 meV

$$p \propto \exp \left(-\frac{E_A}{2k_BT}\right).$$

Here, $k_B$ is the Boltzmann’s constant, and $T$ the absolute temperature. This $E_A$ value is much smaller than those in Al-doped BaSi2 ($E_A = 50$ and 140 meV). Such a shallow acceptor level of 23 meV could be the reason for heavily p-type doping in sample E. The activation energies of as-grown and RTA-treated samples E and G are almost the same, which were roughly 20 meV. But for other samples such as sample C, the activation energy became more than 70 meV after the RTA treatment. Thus, further systematic studies are necessary in order to understand fully the dependences of the activation energy on B concentration and RTA duration. Regarding Ga-, Cu-, and Ag-doped BaSi2 films, variable range hopping conduction of carriers was observed, while conventional band transport of carriers was observed for Sb- and In-doped BaSi2. In order to exclude the possibility of variable range hopping in B-doped BaSi2, we plotted the logarithmic dependence of resistivity on both $1/T^{1/2}$ and $1/T^{1/4}$ for B-doped BaSi2 (sample E) in Fig. 2(b). Non-linear behaviors were observed, meaning that the carrier transport cannot be explained by variable range hopping, differently from Ga-, Cu-, and Ag-doped BaSi2. Similar results were obtained for other samples. The temperature dependence of mobility for sample E was inserted. The mobility decreased with increasing temperature, meaning that the phonon scattering dominates in sample E. Actually, the scattering mechanism differed between samples, depending on B concentrations. Detailed studies will be reported elsewhere.

We next performed the RTA on all the samples to electrically activate the B atoms. Figure 3(a) presents the dependence of hole concentrations on RTA duration, $t_{\text{RTA}}$, for samples A, C, E, and G. The hole concentration increased from $8.5 \times 10^{16}$ to $6.0 \times 10^{17}$ cm$^{-3}$ for sample A when $t_{\text{RTA}}$ was increased from 0.5 to 2 min, similarly from $5.0 \times 10^{17}$ to $1.6 \times 10^{19}$ cm$^{-3}$ for sample C. These results revealed that RTA is a very effective means to activate the B atoms in BaSi2, as reported in other materials such as Si, GaAs, GaN, and ZnO. For sample E, the hole concentration increased from $1.0 \times 10^{19}$ to $2.7 \times 10^{19}$ cm$^{-3}$ after the 1 min RTA but decreased down to $1.1 \times 10^{19}$ cm$^{-3}$ by further annealing. This might be caused by low $T_S$ for too large $N_B$ in sample E. We therefore decided to increase $T_S$ from 600 to 650 °C and decreased $N_B$ from $1 \times 10^{22}$ to $2 \times 10^{21}$ cm$^{-3}$ for sample G. As shown in Fig. 3(a), the hole concentration was increased much further up to $2.0 \times 10^{20}$ cm$^{-3}$ after the 2 min RTA in sample G. This value is the highest ever achieved for BaSi2, indicating that higher $T_S$ improved the electrical activation efficiency of B atoms. The activation efficiency of B atoms in sample G can thus be estimated, that is, $p/N_B = 2.0 \times 10^{20}/2 \times 10^{21} \approx 10\%$ after the 2 min RTA. The obtained $p$ and hole mobility $\mu_p$ were summarized in Fig. 3(b). As the hole concentration increased, the mobility decreased. This trend is usually predicted by ionized

![FIG. 1. SIMS depth profiles of B atoms in samples A, C, and E, grown at $T_B = 1350, 1450$, and 1550 °C, respectively.](image1)

![FIG. 2. (a) Temperature dependence of hole concentration and (b) logarithmic dependence of resistivity on $1/T^{1/2}$ and $1/T^{1/4}$ for sample E, B-doped p-BaSi2 grown with $T_B = 1550$ °C. Temperature dependence of mobility for sample E was inserted.](image2)
impurity scattering in conventional semiconductors. As can be seen, the hole concentration was controlled in the range between $10^{17}$ and $10^{20}$ cm$^{-3}$ for B-doped $p$-BaSi$_2$ grown at $T_B = 1350-1575$ °C. The solid line is a guide to the eye.

In conclusion, we have achieved heavily $p$-type doping over $10^{20}$ cm$^{-3}$ in B-doped BaSi$_2$ by MBE. The acceptor level was estimated to be approximately 23 meV. The RTA treatment at 800 °C enhanced the electrical activation of doped B atoms, thereby increasing the hole concentrations up to $2.0 \times 10^{20}$ cm$^{-3}$.

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