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Citation: Appl. Phys. Lett. **102**, 112107 (2013); doi: 10.1063/1.4796142
View online: http://dx.doi.org/10.1063/1.4796142
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i11
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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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(Received 26 December 2012; accepted 8 March 2013; published online 19 March 2013)

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 1×10^{20} cm^{-3} were achieved via dopant activation using RTA at 800 °C in Ar. The activation efficiency was increased up to 10%. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4796142]

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.[1,2] It has an indirect band gap of approximately 1.3 eV, matching the solar spectrum.[3–5] In addition, $BaSi_2$ has a large absorption coefficient of 3×10^4 cm^{-1} at 1.5 eV,[5] much larger than crystalline Si. Recent reports on high photoresponsivity and large internal quantum efficiencies exceeding 70% have spurred interest in this material.[6–8] The remaining process was the formation of p-type $BaSi_2$ on the undoped n-type $BaSi_2$ layer ($n = 5 \times 10^{15}$ cm^{-3}) to complete the $BaSi_2$ *pn* junction diode.[4] 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.[9] In line with this theoretical expectation, Sb-doped $BaSi_2$ exhibits n-type conductivity, while In-, Al-, and Ag-doped $BaSi_2$ exhibit p-type conductivity.[10–12] 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.[10] In contrast, the hole concentration was limited up to 3–4 $\times 10^{17}$ cm^{-3} at RT in In-, Al-, and Ag-doped $BaSi_2$ layers.[10,11] 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.[10–12] Briefly, a 10-nm-thick $BaSi_2$ epitaxial film was first grown by reactive deposition epitaxy on floating-zone (FZ) n-Si(111) substrates ($\rho > 1000$ Ω·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 relatively uniformly distributed within the $BaSi_2$ layers. Their average B concentration, N_B, was approximately 3×10^{20}, 2×10^{21}, and 1×10^{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

TABLE I. Sample preparation: Growth temperature (T_S), B temperature (T_B), measured hole concentration (p), and mobility (μ_p) are shown.

Sample	T_S (°C)	T_B (°C)	p (cm^{-3})	μ_p (cm^2/V·s)
A	600	1350	…	…
B	600	1400	…	…
C	600	1450	…	…
D	600	1500	…	…
E	600	1550	1.0×10^{19}	6.3
F	600	1575	2.5×10^{18}	8.3
G	650	1450	6.5×10^{19}	0.8

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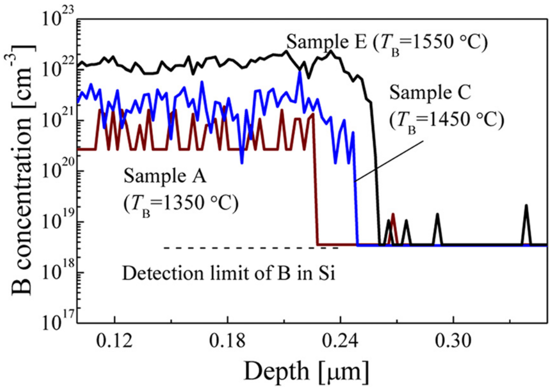

FIG. 1. SIMS depth profiles of B atoms in samples A, C, and E, grown at $T_B = 1350$, 1450, and 1550 °C, respectively.

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.[13]

B-doped as-grown $BaSi_2$ 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 $1.0 \times 10^{19}\,\text{cm}^{-3}$ at RT and decreased with decreasing temperatures. The acceptor level, E_A, calculated using Eq. (1) was 23 meV

$$p \propto \exp\left(-\frac{E_A}{2k_B T}\right). \tag{1}$$

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 $BaSi_2$ ($E_A = 50$ and 140 meV).[11] 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 $BaSi_2$ films, variable range hopping conduction of carriers was observed, while conventional band transport of carriers was observed for Sb- and In-doped $BaSi_2$.[12] In order to exclude the possibility of variable range hopping in B-doped $BaSi_2$, we plotted the logarithmic dependence of resistivity on both $1/T^{1/2}$ and $1/T^{1/4}$ for B-doped $BaSi_2$ (sample E) in Fig. 2(b). Non-linear behaviors were observed, meaning that the carrier transport cannot be explained by variable range hopping,[14–16] differently from Ga-, Cu-, and Ag-doped $BaSi_2$. 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.

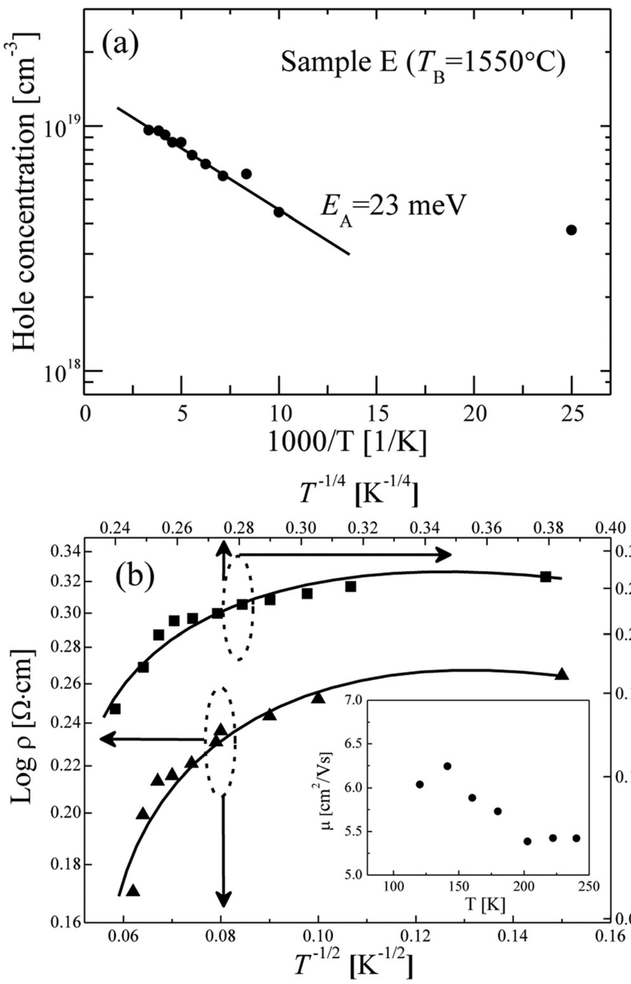

FIG. 2. (a) Temperature dependence of hole concentration and (b) logarithmic dependence of resistivity on $1/T^{1/2}$ and $1/T^{1/4}$ for sample E, B-doped *p*-$BaSi_2$ grown with $T_B = 1550$ °C. Temperature dependence of mobility for sample E was inserted.

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_{RTA}, for samples A, C, E, and G. The hole concentration increased from 8.5×10^{16} to $6.0 \times 10^{17}\,\text{cm}^{-3}$ for sample A when t_{RTA} was increased from 0.5 to 2 min, similarly from 5.0×10^{17} to $1.6 \times 10^{19}\,\text{cm}^{-3}$ for sample C. These results revealed that RTA is a very effective means to activate the B atoms in $BaSi_2$, as reported in other materials such as Si, GaAs, GaN, and ZnO.[17–20] For sample E, the hole concentration increased from 1.0×10^{19} to $2.7 \times 10^{19}\,\text{cm}^{-3}$ after the 1 min RTA but decreased down to $1.1 \times 10^{19}\,\text{cm}^{-3}$ 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 1×10^{22} to $2 \times 10^{21}\,\text{cm}^{-3}$ for sample G. As shown in Fig. 3(a), the hole concentration was increased much further up to $2.0 \times 10^{20}\,\text{cm}^{-3}$ after the 2 min RTA in sample G. This value is the highest ever achieved for $BaSi_2$, 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, $p/N_B = 2.0 \times 10^{20}/2 \times 10^{21} \cong 10\%$ after the 2 min RTA. The obtained p and hole mobility μ_p were summarized in Fig. 3(b). As the hole concentration increased, the mobility decreased. This trend is usually predicted by ionized

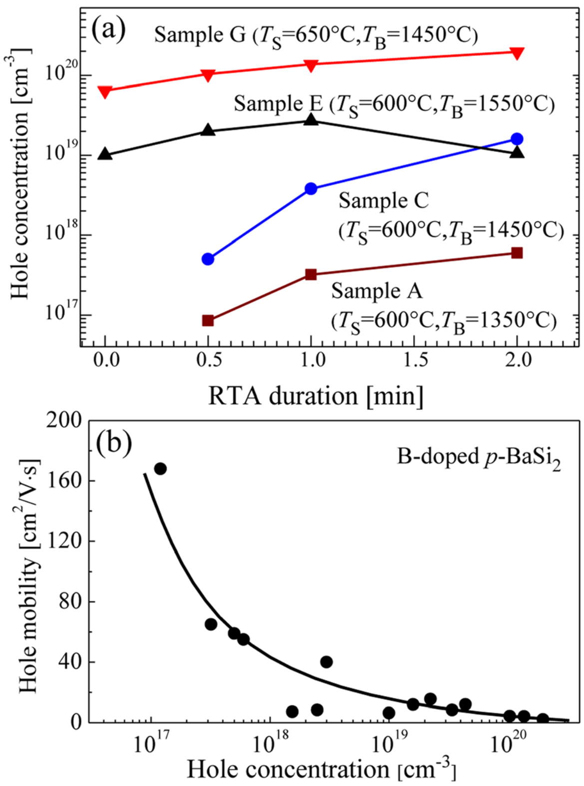

FIG. 3. (a) Dependences of hole concentration on t_{RTA} for samples, A, C, E, and G, and (b) relationship of measured mobilities and hole concentrations for B-doped p-BaSi$_2$, grown at $T_B = 1350$–$1575\,°C$. The solid line is a guide to the eye.

impurity scattering in conventional semiconductors. As can be seen, the hole concentration was controlled in the range between 10^{17} and $10^{20}\,cm^{-3}$ at RT by changing the temperature of the B Knudsen cell crucible.

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 $2.0 \times 10^{20}\,cm^{-3}$.

This work was supported in part by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency.

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