Control of electrical properties of BaSi₂ thin films by alkali-metal doping using alkali-metal fluorides

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Abstract

Exploration of impurity elements for carrier density control is important for device application of the BaSi₂ semiconductor, which is a promising candidate for an earth-abundant solar cell absorber. In this study, we have investigated the doping of BaSi₂ films with alkali metals (Li, Na, and K) by deposition of alkali-metal fluorides followed by rapid thermal annealing. Electrical characterization by Hall measurement shows that LiF treatment increases electron density in BaSi₂ up to 10^{20} cm^{-3} after annealing at 500 °C while NaF and KF treatments have limited effects with electron densities lower than 10^{18} cm^{-3} . The mechanisms of electrical property modification are discussed from structural viewpoints. Secondary ion mass spectroscopy shows that Li atoms slightly diffuse into the film at 400 °C by prolonged

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annealing, which nevertheless does not accordingly increase the carrier density. Formation of barium fluoride, oxide, and silicon at 500 °C, which is revealed by energy-dispersive X-ray and Raman spectroscopies, brings about the conclusion that a high temperature is needed for the dissociation of LiF through the reaction with BaSi₂ and the incorporation of Li atoms probably into the interstitial sites of BaSi₂, which would generate electrons. On the other hand, Na and K atoms are found to evaporate at the same time as the dissociation of NaF and KF, respectively, evidenced by energy-dispersive X-ray spectroscopy. BaF₂ formation accompanied by the NaF dissociation is detected by X-ray diffraction.

Keywords: Barium silicide, Silicide semiconductor, Impurity doping, Electrical property, Alkali metal

1. Introduction

The BaSi₂ semiconductor is attracting much attention as a light-absorbing material for thin-film solar cells because of excellent optoelectronic properties as well as the abundance of constituent elements in the earth's crust. The optical band gap of 1.13–1.34 eV [1–3] and high absorption coefficients, reaching $3 \times 10^4 \text{ cm}^{-1}$ for a photon energy of 1.5 eV [3], can receive the benefit of high theoretical efficiency with a thin film of a few micrometers. In addition, long minority-carrier diffusion length of approximately 10 μm [4] and minority-carrier lifetime up to 11 μs [5] in epitaxial films grown on Si(111) wafers also suggest the possibility of high efficiency BaSi₂ devices. This characteristic of having both large absorption coefficients and long carrier diffusion length are a great merit of BaSi₂ [6]. In combination with the

resource abundance, large-scale deployment of high-efficiency solar cells can be expected with BaSi₂.

Alkali metal doping by means of the deposition of alkali-metal fluorides is an interesting technique. The efficiency of Cu(In,Ga)Se₂ solar cells can be significantly improved by the post-deposition NaF and KF treatments through defect passivation [7–10], which is why this technique is extensively studied and introduced into solar-cell processes [9, 10]. Doping of BaSi₂ with alkali metals is also interesting because of various potential benefits. For example, it is reported that p-type semiconducting solid solution may be formed by the substitution of K or Cs for Ba⁽¹⁾ sites in BaSi₂ in a first-principles calculation study [11]. P-type doping of BaSi₂ may therefore be possible by the alkali-metal-fluoride treatment, which is essential to form a pn junction. N-type doping is also conceivable because the ionic radius of Li is almost same as Cu [12], which is a donor in BaSi₂ [13, 14]. Besides, since the melting points of alkali metals are low (≤ 181 °C), low temperature doping can be expected, which enables to avoid problems involving high-temperature processes such as cracking [15] and dopant diffusion [16]. The alkali-metal-fluoride treatment therefore has a potential as a simple and useful technique to modify the properties of BaSi₂.

Experimental demonstration of the alkali-metal-fluoride treatment has, however, never been reported so far. It remains completely unknown whether and how BaSi₂ is doped with the alkali metals. In addition, the reactivity of fluorides with BaSi₂ needs experimental investigation. Thus, in this study, we have investigated the alkali-metal-fluoride (LiF, NaF, and KF) treatment of BaSi₂ films. Modification of electronic properties will be revealed, the

underlying mechanism of which is elucidated on the basis of related structural change. It is shown that Li impurity can be a useful n-type dopant with high electron densities up to 10^{20} cm^{-3} while it is found difficult to dope BaSi₂ with Na and K due to their evaporation.

2. Experimental method

An undoped BaSi₂ epitaxial film was grown on n-type Si(111) substrate ($> 1000 \Omega\cdot\text{cm}$) by reactive deposition epitaxy (RDE) followed by molecular beam epitaxy (MBE) using an ion-pumped MBE system equipped with solid sources of Ba and Si. The RDE is the process to produce a thin template BaSi₂ layer by depositing Ba atoms on a hot Si substrate. The BaSi₂ epitaxial film with a thickness of 320 nm was subsequently formed by MBE, which is the co-deposition of Ba and Si atoms on the template layer. The details of the growth procedure are found elsewhere [17, 18].

Powders of alkali-metal fluorides (LiF, NaF, and KF, purchased from Nacalai Tesque) were thermally evaporated in a vacuum chamber and deposited on the BaSi₂ film. The purities of the LiF, NaF, and KF powders were 99.5, 99.5, and 99.9% with major metallic impurities of Li₂SiF₆ ($< 0.1\%$), SiF₆ ($< 0.05\%$), and Na ($< 0.1\%$), respectively. The film thicknesses were set to 10–23 nm, depending on the alkali metal species, by varying the weight of source powders, so that the alkali-metal concentration averaged by the BaSi₂ film thickness could be $2 \times 10^{21} \text{ cm}^{-3}$. The alkali-metal fluorides/BaSi₂/Si samples were subsequently subjected to rapid thermal annealing (RTA) at 300–500 °C for 1–4 min under high-purity (99.9999%) Ar flow.

The electrical properties of the samples were investigated by Hall mea-

surement (TOYO ResiTest8308) with the van der Pauw method and the four-point probe resistivity measurement. For Hall measurement, Al contacts were deposited on the surface by radio-frequency magnetron sputtering at room temperature. The carrier mobility was analyzed using the resistivity values determined by four-point probe measurement since the resistivity values from the van der Pauw method sometimes deviated due to the Schottky nature of the contacts. The accuracy of the Hall voltage was assured by the linear dependence of Hall voltage on the input current. The structure of the samples was characterized by Raman spectroscopy (Renishaw inVia Raman microscope) with a diode laser ($\lambda = 488$ nm), scanning electron microscopy (SEM, JEOL JSM-7001FA) equipped with an energy-dispersive X-ray spectroscopy (EDX) system, secondary ion mass spectroscopy (SIMS, CAMECA IMS-7F) with a 5 keV O^+ primary ion beam, and X-ray diffraction analysis (XRD, Bruker Discover D8). The acceleration voltage of SEM and EDX analyses was 15 kV. Analyzed areas of EDX were $121 \times 91 \mu m^2$ rectangles if not indicated. XRD analysis was performed with the $2\theta-\omega$ configuration using the Cu $K\alpha$ radiation monochromated by a two-bounce Ge(220) monochromator.

3. Results and discussion

3.1. Electrical properties and structural modification

The Hall measurement has revealed that the $BaSi_2$ films treated with alkali-metal fluorides have n-type conductivity. Figure 1 shows the electron density (n) averaged by the $BaSi_2$ film thickness and average mobility (μ). Note that parallel conduction through both the $BaSi_2$ film and the Si

Figure 1: Electron density (n) and mobility (μ) in the BaSi_2 samples treated with alkali-metal fluorides. The n and μ values of undoped BaSi_2 film [19] is also displayed with short dashed lines.

substrate could occur during the measurement. According to the current-path analysis similar to that in Ref. [20], substrate conduction is dominant when $n < 1 \times 10^{18} \text{ cm}^{-3}$. In particular, assuming a conducting layer thickness of 600 μm (substrate), n values of $2\text{--}5 \times 10^{15} \text{ cm}^{-3}$ with μ of around $1.2 \times 10^3 \text{ cm}^2/\text{V}\cdot\text{s}$ correspond to a resistivity of $2\text{--}5 \times 10^3 \Omega\cdot\text{cm}$. This means that we measured the substrate properties for the samples annealed at 300 $^\circ\text{C}$. With the decrease in BaSi_2 resistivity, the contribution of film conduction increases. For $n = 1 \times 10^{20} \text{ cm}^{-3}$, the resistance ratio of BaSi_2 to Si becomes 0.24. The increase of n by annealing is the evidence that the introduced impurities from the alkali-metal fluorides serve as donors in BaSi_2/Si samples. Furthermore, the decreasing tendency of μ with increasing n coincides with reported n-type BaSi_2 films doped with Cu [21], Ga [21], P [22], and Sb [23].

Among the alkali-metal fluorides studied, LiF treatment has been found to be most efficient for electron generation, as shown in Fig. 1. n reaches $1 \times 10^{19} \text{ cm}^{-3}$ by RTA at 400 $^\circ\text{C}$ for 1 min, and further increases to $3 \times 10^{20} \text{ cm}^{-3}$ at 500 $^\circ\text{C}$. This value of $3 \times 10^{20} \text{ cm}^{-3}$ is similar to the highest n value reported for Sb-doped BaSi_2 films [23]. LiF may, therefore, be used as an alternative donor impurity.

On the other hand, n values of NaF- and KF-treated samples are significantly smaller than the LiF-treated ones. By RTA up to 400 $^\circ\text{C}$, n does not significantly change. At 500 $^\circ\text{C}$, n increases to $3\text{--}4 \times 10^{17} \text{ cm}^{-3}$, but it is one thousand times smaller than the LiF-treated sample.

Not only the RTA temperature but also RTA duration can influence the dopant activation. As shown in Fig. 1(b), n of LiF-treated samples doubles by increasing RTA duration from 1 to 2 min at 400 $^\circ\text{C}$. Longer annealing for

4 min, however, does not significantly change n . Two reasons are conceivable for this phenomenon. One is that the solubility limit has been reached by RTA for 2 min. It is, however, not so probable that a solubility limit increases by more than ten times with the increase of temperature by one hundred degrees to 500 °C. The other one is that there is a mechanism to limit the electrical activation of dopant. For example, the dissociation of LiF may need high temperatures.

Figure 2 shows the Raman spectra of the BaSi₂ films treated with alkali-metal fluorides at 400 and 500 °C for 1 min together with annealed films without fluorides. The 400 °C-annealed samples exhibit five peaks irrespective of alkali-metal-fluoride treatment, which are attributed to the vibration of discrete [Si₄]⁴⁻ tetrahedral anions in BaSi₂ [24]. Thus, the film structure is retained up to annealing temperatures of 400 °C. On the other hand, at 500 °C, transverse optical (TO) phonon mode of crystalline Si is observed at 515–522 cm⁻¹ in addition to BaSi₂. This is partly because of oxidation of BaSi₂ into barium oxide and Si due to a trace amount of oxygen in the atmosphere [25]. Here, it should be noted that the integrated-intensity ratios of Si(TO) to $\nu_1(A_1)$ of LiF-, NaF-, and KF-treated samples (0.29–0.99) are significantly higher than undoped one (0.12). This suggests that LiF-, NaF-, and KF-treated samples decompose at 500 °C partly due to alkali-metal fluorides. Since n increases at 500 °C (Fig. 1), the decomposition of BaSi₂ may be related to the electrical property variation.

Elemental compositions of the samples were analyzed by EDX. Figure 3 displays the EDX spectra of the LiF-, NaF-, and KF-treated BaSi₂ samples annealed at 300–500 °C. The analyzed areas are 121 × 91 μm² rectangles.

Figure 2: Raman spectra of (a) undoped, (b) LiF-, (c) NaF-, and (d) KF-treated BaSi_2 samples annealed at 400 and 500 $^\circ\text{C}$ for 1 min. ν_1 , ν_2 , and ν_3 denote the vibration modes of $[\text{Si}_4]^{4-}$ anions corresponding to the symmetry elements A_1 , F_2 , and E , respectively.

Figure 3: EDX spectra of (a) LiF-, (b) NaF-, and (c) KF-treated BaSi₂ samples annealed at 300–500 °C for 1 min. The acceleration voltage of electron was 15 keV.

LiF-treated samples [Fig. 3(a)] show Ba, Si, and F peaks together with contaminant elements (C and O). Small Al peaks derive from the Al sample stage of EDX. Li is not detected because it is undetectable by EDX. With increasing RTA temperature, no significant change of the spectrum is observed. On the other hand, in NaF- and KF-treated samples, Na and K peaks are observed. And, it should be noted that the Na $K\alpha$ peak almost disappears after RTA at 400 and 500 °C. Most of Na atoms are therefore lost by RTA at 400 °C and above. The K $K\alpha$ peaks are observed after RTA at 300 and 400 °C. At 500 °C, however, the peak disappears similarly to Na. These losses of Na and K may account for lower n values in NaF- and KF-treated samples than LiF-treated ones in Fig. 1.

3.2. Mechanism of electrical property variation

Electrical characterization has revealed that the electrical properties can be modified by alkali-metal-fluoride treatment. It is, however, ambiguous what element serves as donor impurity and why the doping efficiency varies depending on the alkali metal species and RTA conditions. The doping mechanism will be elucidated in this subsection mainly on the basis of structural characterization.

3.2.1. LiF doping

The doping mechanism of Li may accord with that of Cu because the ionic radius of Li almost coincides with Cu. The radii of monovalent four-coordinated Li and Cu ions are, for example, 0.59 and 0.6 Å, respectively (radii for six-fold coordination are also almost same.) [12]. The Cu impurity is reported to act as donor in BaSi₂ [13, 14], which has been theoretically

Figure 4: SIMS profiles of ^7Li , ^{28}Si , and ^{138}Ba in the LiF-treated BaSi_2 samples annealed at 400 °C for 1–4 min.

supported by a first-principles calculation [26]. According to these reports, Cu atoms are probably incorporated into the interstitial $4c$ sites of BaSi_2 where a Cu atom is surrounded by three Si atoms [26], and emit electrons. Li atoms may behave similarly to Cu as donor impurity at the interstitial sites in BaSi_2 .

A significant amount of donor impurity from LiF is activated at 400 °C as shown in Fig. 1. The activation ratio is, however, less than 1% (estimated from the amount of deposited LiF), and it does not increase considerably by elongated annealing [Fig. 1(b)]. Figure 4 shows the SIMS profiles of ^7Li ,

^{28}Si , and ^{138}Ba in the LiF-treated samples annealed at 400 °C. The region with high ^{138}Ba intensities corresponds to the BaSi_2 layer. The original horizontal axis of sputtering time was converted linearly to the depth, using the BaSi_2 layer thickness. At an RTA temperature of 400 °C, Most of Li atoms are found to segregate to the surface and the BaSi_2 –Si interface up to an RTA duration of 4 min. Interface segregation is presumably due to the fast diffusion through the domain boundaries [27–29]. Low activation ratio of the dopant at 400 °C may be related to this Li segregation.

With increasing RTA duration, ^7Li intensity around a depth of 100 nm seems to be enhanced, as indicated by dotted circles and an arrow in Fig. 4. This Li insertion may be related to the lattice diffusion of Li. Despite the Li insertion, however, n is not considerably enhanced. This result suggests that LiF is not effectively dissociated and incorporated into the BaSi_2 lattice at this temperature.

By RTA at 500 °C, n increases by more than ten times compared with 400 °C-annealed samples. As shown in SEM pictures in Fig. 5, particles are produced on the surface at 500 °C. While small particles less than 300 nm long, probably of LiF, are observed on the surface annealed at 400 °C, larger particles of a few micrometers are present after RTA at 500 °C. These large particles can be observed also in the cross-sectional image, as shown in Fig. 5(d). EDX was used to investigate the composition of the particulate product. As shown in Fig. 5(e), the particulate product contains more fluorine, oxygen and less silicon atoms than those in the flat film region. Considering that EDX signal comes also from outside the scanned region, the particulate product is probably fluoride and oxide of barium. Oxygen

Figure 5: SEM images of LiF-treated samples annealed at 400 and 500 °C for 1 min. EDX spectra of selected areas of 500 °C-annealed sample are also displayed. The acceleration voltage of electron was 15 keV.

atoms presumably came from the quartz sample holder used for RTA or are impurity of Ar gas. Due to the formation of the particles, the thickness of flat film region was decreased to 270 nm. Another influence of the particles is an enhanced surface roughness, which considerably deteriorated the spatial resolution of SIMS. Nevertheless, existence of Li atoms in the film was confirmed by SIMS. In addition, it should be recalled that crystalline Si is formed at 500 °C, as observed in the Raman spectra of Fig. 2(a). From these results, enhanced activation of dopant at 500 °C is probably due to the promoted dissociation of LiF and formation of interstitial Li atoms in BaSi₂ through the following chemical reaction: $\text{BaSi}_2 + \text{LiF} + \text{O}_2 \rightarrow \text{Ba-F-O} + \text{Si} + \text{Li}_i$. Here, Li_i denotes the interstitial Li atom in BaSi₂.

To summarize the above results, it is most likely that Li impurity works as donor in BaSi₂. When using LiF as Li source, a high temperature of 500 °C is necessary to dissociate LiF and effectively dope BaSi₂ with Li. Formation of by-products such as barium fluoride, oxide and crystalline silicon is a drawback of using LiF.

3.2.2. NaF and KF doping

The NaF- and KF-treated samples show by far lower n values than LiF-treated ones (Fig. 1). Two mechanisms are conceivable for this result. One is that Na and K atoms have larger ionic radii than Li, which prevent effective incorporation of Na and K atoms into the interstitial sites in BaSi₂. The radii of monovalent four-coordinated Na and K ions are 0.99 and 1.37 Å, larger than Li (0.59 Å) [12]. Na insertion into the interstitial sites is actually reported to be energetically unfavorable [30]. Instead of interstitial doping, it is theoretically predicted that K substitution of Ba⁽¹⁾ sites is possible, which

would show p-type conductivity [11]. Such substitutional doping has not been observed under the present experimental conditions.

The other possible mechanism of low dopant activation is the loss of Na and K atoms, as has been shown in Fig. 3. The losses of Na and K are probably because of their evaporation. At 400 °C, the equilibrium vapor pressures of Na and K are 40 and 5×10^2 Pa, respectively, which are more than three orders of magnitude higher than Li (1×10^{-2} Pa) [31]. Existence of K after RTA at 400 °C despite higher vapor pressure than Na may be because the dissociation of KF may need higher activation energy than NaF. Thus, smaller variation of electrical properties by NaF and KF doping is largely due to the evaporation loss of Na and K at 400 °C and above.

At the same time as the evaporation of Na and K, the F atoms possibly react with BaSi₂ to produce BaF₂. Figure 6 shows 2θ - ω XRD patterns of NaF-treated BaSi₂ samples. At 300 °C, the $h00$ peaks of BaSi₂ are observed, according to the a -axis-oriented epitaxy on the Si(111) substrate, together with the substrate peaks. At higher temperatures of 400 and 500 °C, in addition to the BaSi₂ and Si peaks, the 111 and 220 diffractions of BaF₂ are observed. This observation supports the coincident fluoridation with alkali metal evaporation. BaF₂ was not detected in the case of KF treatment. This may be because of random orientation of BaF₂. Based on the above results, a probable chemical reaction is $2\text{NaF (2KF)} + \text{BaSi}_2 = \text{BaF}_2 + 2\text{Na}\uparrow (2\text{K}\uparrow) + 2\text{Si}$. Formation of Si was detected by Raman spectroscopy, as shown in Fig. 2. One exception is the NaF-treated sample at 400 °C, which does not exhibit a Si peak.

On the basis of the above results, the usage of NaF and KF is not efficient

Figure 6: 2θ - ω XRD patterns of NaF-treated BaSi_2 samples annealed at 300–500 °C. The asterisk symbol represents the multiple diffraction from the Si substrate.

means either to modify the electrical properties of BaSi₂ nor to dope BaSi₂ with alkali metals. A small increase of n at 500 °C [Figs. 1(b) and (c)] may be attributed to the deviation of composition from the stoichiometry due to the Ba deficiency caused by fluoridation. For the doping with Na and K, other chemical forms than fluorides should be used. For example, metallic Na and K deposition and post annealing in the vacuum chamber would be an alternative method.

4. Conclusion

We have studied the LiF, NaF, and KF treatment of BaSi₂ films by means of thermal evaporation followed by RTA. It has been found that a high n value exceeding 10^{20} cm⁻³ can be realized by LiF treatment with RTA at 500 °C for 1 min, while NaF and KF are not effective substances for electrical property modification. High n possibly derives from Li atoms inserted into the interstitial sites of BaSi₂. A High temperature of 500 °C is necessary to dissociate LiF and effectively dope BaSi₂ with Li. Formation of by-products such as barium fluoride, oxide, and silicon is a drawback of LiF treatment. When using NaF or KF, evaporation of Na and K occurs at the same time as the dissociation, which prevents the doping with Na and K. The dissociation reaction also produces BaF₂ and Si.

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