N-type doping of BaSi₂ epitaxial films by arsenic ion implantation through a dose-dependent carrier generation mechanism

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Abstract

Arsenic doping by ion implantation and thermal annealing of the BaSi₂ epitaxial films grown on Si(111) substrates has been studied. Raman spectroscopy shows that a structural change can occur by annealing at 500 °C after As implantation with as high dose as $1.0 \times 10^{15} \text{ cm}^{-2}$. This structural change is shown to result in the formation of an altered layer after annealing at the surface by cross-sectional scanning electron microscopy. Secondary ion mass spectroscopy reveals that the altered layer contains a significant amount of O atoms. With the altered layer present, average electron density up to $6.0 \times 10^{19} \text{ cm}^{-3}$ has been realized, which is revealed by the Hall measurement. On the other hand, without the altered layer, high resistance of the BaSi₂ layer prevented the electrical characterization. Current path is

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discussed by theoretically calculating the band alignment and resistance, and possible highest electron density without the altered layer is extracted to be less than $2 \times 10^{17} \text{ cm}^{-3}$.

Keywords: Barium silicide, Silicide semiconductor, Epitaxial film, Arsenic impurity, Ion implantation

1. Introduction

Orthorhombic BaSi₂ is attracting much attention as an active-layer material for thin-film solar cells because of an appropriate band gap (1.3 eV [1]) for single-junction solar cells and a high absorption coefficient, reaching $3 \times 10^4 \text{ cm}^{-1}$ for a photon energy of 1.5 eV [1]. The abundance of constituent elements in the earth's crust is also preferable for large-scale production. In addition, well-crystalline *a*-axis-oriented films can be grown on either Si(111) or Si(100) substrate [2, 3]. Long bulk minority-carrier lifetime up to 14 μs in the annealed epitaxial films [4] suggests the possibility of high efficiency BaSi₂ devices.

For the fabrication of a desired device, it is important to explore the impurity elements for BaSi₂ which can yield a wide range of carrier densities. Sb is a promising donor impurity for BaSi₂, which can control the electron density in the wide range of 10^{17} – 10^{20} cm^{-3} [5]. From the group-V elements, P doping has also been studied [6–8]. The electron density of the P-doped BaSi₂ films is, however, limited up to the order of 10^{18} cm^{-3} [6, 8]. In this study, to further explore the dopants of BaSi₂ from the group V, we focused on As impurity. Ion implantation is useful for doping with controlled dopant profile, as effectively used in the ion implantation doping of P [7, 8]. The

purpose of the present paper is to investigate the effects of As doping by ion implantation on the structure and electrical properties of the BaSi₂ epitaxial film.

2. Experimental methods

The *a*-axis-oriented BaSi₂ films were grown on p-type Si(111) substrates ($\geq 1000 \text{ } \Omega \cdot \text{cm}$ in resistivity) 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 (500 °C in this study). The BaSi₂ epitaxial films with the thickness of 300 and 400 nm were subsequently formed at 580 °C by MBE, which is the co-deposition of Ba and Si atoms on the template layer. The grown films were implanted with As⁺ ions at room temperature at energies of 45 and 150 keV with doses of 1.0×10^{13} – $1.0 \times 10^{15} \text{ cm}^{-2}$, which correspond to average As densities of 2.5×10^{17} – $3.3 \times 10^{19} \text{ cm}^{-3}$. As-implanted films were subsequently subjected to lamp annealing (MILA-5000, ULVAC) at 500 °C for 30–1920 s under high-purity (99.9999 %) Ar flow. The heating rate was 40 K/s. Samples were characterized by Raman spectroscopy (Nanofinder, Tokyo Instruments) with an Ar⁺ ion laser ($\lambda = 488 \text{ nm}$), scanning electron microscopy (SEM; JSM-7001FA, JEOL), X-ray diffractometry (XRD; Discover D8, Bruker) with Cu *K* α radiation, secondary ion mass spectroscopy (SIMS; IMS-7 F, CAMECA) with a 15 keV Cs⁺ primary ion beam, and the Hall measurement (HEM-2000, EGK) with the van der Pauw method. The analysis area of SIMS was a 30- μm -diameter spot. For the Hall measurement, Al ohmic contacts were

Figure 1: Effects of As implantation with an energy of 150 keV and subsequent annealing at 500 °C on the Raman spectrum of BaSi₂. The film thickness of BaSi₂ is 400 nm.

deposited on the BaSi₂ surface by radio-frequency magnetron sputtering at room temperature.

3. Results and discussion

Fig. 1 shows the Raman spectra after As implantation and subsequent annealing at 500 °C. Peaks from the as-grown film in the range of 280–500 cm⁻¹ are attributed to the vibration of discrete [Si₄]⁴⁻ tetrahedral anions in the BaSi₂ structure [9]. These peaks become almost invisible after As implantation with a dose of 1.0×10^{15} cm⁻², while they are clearly observed

with $1.0 \times 10^{14} \text{ cm}^{-2}$ of As. The disappearance of the Raman peaks is probably because of partial destruction of the BaSi_2 crystal structure around the film surface, similarly to P implantation [7, 8].

After annealing the As-implanted film at 500 °C for 120 s, sharp peaks of BaSi_2 are observed, indicating that the implantation damage can be recovered at 500 °C within 120 s. The annealing duration as short as 30 s is enough to remove the implantation damage, which was confirmed on the 300-nm-thick film implanted at an energy of 45 keV. This result agrees with our previous report on P implantation [8]. With increased annealing durations up to 1920 s, unidentified peaks (165, 317, and 418 cm^{-1}) indicated by arrows appear and become larger, which suggests the formation of another phase in the film. These peaks were observed only with the highest dose, $1.0 \times 10^{15} \text{ cm}^{-2}$, of this study.

To investigate the structure of the unidentified phase formed by As doping, the samples were also analyzed by 2θ - ω XRD. The 200, 400, and 600 diffractions of BaSi_2 as well as diffractions from the Si substrate were observed, as shown in Fig. 2. No other peaks related to the phase change were, however, observed. The produced phase may, hence, be microcrystalline or amorphous, or a thin layer around the surface.

Fig. 3 shows SIMS depth profiles after As implantation at an energy of 150 keV with a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$ and subsequent annealing at 500 °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. Since the Si_3O ions whose molecular weight is equal to $^{75}\text{As}^{28}\text{Si}$ are counted together with $^{75}\text{As}^{28}\text{Si}$, $^{75}\text{As}^{28}\text{Si}$ has high

Figure 2: 2θ - ω XRD patterns of (a) the BaSi₂ film implanted with $1.0 \times 10^{15} \text{ cm}^{-2}$ of As and annealed at 500 °C for 1920 s and (b) the as-grown film. The film thickness of BaSi₂ is 400 nm. The asterisk symbol denotes the multiple diffraction from the Si substrate.

background also in the Si layer. Considering the high background level up to 10^2 cps, most of As atoms are presumably present in the BaSi₂ layer.

With increasing the annealing duration, As atoms are observed to diffuse to the BaSi₂/Si interface. Most of the As atoms, however, remain within 200 nm from the surface even after annealing for 1920 s. The $^{75}\text{As}^{28}\text{Si}$ curves of the annealed films seem jagged in the BaSi₂ layer, suggesting that the implanted As atoms are clustered after annealing, which may have retarded the diffusion. It should also be noted that the intensity of ^{18}O becomes higher around the surface with increasing annealing duration. Two mechanisms are possible for this ^{18}O increase. One is the out-diffusion of O from the inside of the sample to the surface, which can be speculated from the reduced ^{18}O intensity inside the sample. Another mechanism is the incorporation of O

Figure 3: SIMS depth profiles of ^{18}O , ^{29}Si , $^{75}\text{As}^{28}\text{Si}$, and ^{138}Ba in the 400 nm films implanted at an energy of 150 keV and annealed at 500 °C up to 1920 s. The As dose is $1.0 \times 10^{15} \text{ cm}^{-2}$.

Figure 4: Cross-sectional SEM image after As implantation at an energy of 150 keV and subsequent annealing at 500 °C for 1920 s. As doses are (a) 1.0×10^{15} and (b) $1.0 \times 10^{14} \text{ cm}^{-2}$.

from the annealing environment. Oxygen atoms may have come from the heated quartz sample stage. This O increase around the surface is observed only with the highest dose, with which the phase change was observed.

Fig. 4 shows the cross-sectional SEM image after As implantation and subsequent annealing at 500 °C for 1920 s. With a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$ [Fig. 4(a)], an altered layer is observed around the surface, while it is not observed with a smaller dose of $1.0 \times 10^{14} \text{ cm}^{-2}$ [Fig. 4(b)]. The unidentified peaks in the Raman spectra in Fig. 1 are, therefore, probably from this altered layer. Furthermore, the thickness of the altered layer is approximately 100 nm, which agrees with the thickness of the region with high ^{18}O intensity

Figure 5: Electron densities determined by the van der Pauw method after As implantation at an energy of 150 keV with a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$ and subsequent annealing at 500 °C.

in the SIMS profile (Fig. 3). From the above results, a compound containing O has been formed by annealing at 500 °C after high-dose As implantation, which corresponds to the altered layer in Fig. 4.

The electrical properties were investigated by the Hall measurement using the van der Pauw method, which has revealed that the majority carrier after As doping is electrons. As revealed in our previous study on P doping [8], current can flow through both the BaSi₂ film and Si substrate. This is because the large difference of electron affinities between BaSi₂ and Si induces an n-type layer in the originally p-type Si substrate around the interface. The total area density of electrons is thus shown, instead of electron density in the film, in Fig. 5. The electron density increases with annealing duration, exceeding the As dose after annealing for 1920 s. Electron generation by As doping, therefore, cannot be explained solely by substitution of As for Si. Furthermore, with smaller doses of $1.0 \times 10^{13} \text{ cm}^{-2}$ and $1.0 \times 10^{14} \text{ cm}^{-2}$, the

Hall measurement was not successful because of current conduction mainly through Si layer, which has been concluded from determined mobility values of $(1.0\text{--}1.1)\times 10^3 \text{ cm}^2/\text{V}\cdot\text{s}$. This is probably due to a high resistance of BaSi_2 layer.

This result that the Hall measurement failed on the films with As doses of 1.0×10^{13} and $1.0 \times 10^{14} \text{ cm}^{-2}$ indicates that the activation mechanism of As depends on its dose. If the activation ratio is independent of As dose, the resistance of the film with $1.0 \times 10^{14} \text{ cm}^{-2}$ of As would be low enough for the Hall measurement after annealing for 480 and 1920 s. This is because the film annealed for 120 s with $1.0 \times 10^{15} \text{ cm}^{-2}$ of As, which has ten times lower electron density than that annealed for 480 s, has a low resistance enough for the Hall measurement. The mechanism of electron generation is therefore dependent on the As dose. Considering the formation of an altered layer with a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$ (Fig. 4), most of the electrons is probably from the altered layer.

To find out the condition that the conduction through the Si layer becomes dominant, the resistance of each layer for electron conduction was calculated from the band alignment [Fig. 6(a)] simulated for a given electron density in the film with a device simulator software (wxAMPS [10]). In the numerical simulation, the effective mass of carriers and the dielectric constant of BaSi_2 were assumed to be the same as those of silicon. Other material parameters such as electron affinity (3.2 eV [11]) and band gap (1.3 eV [12]) were found from the literature. The electron mobility values in the BaSi_2 layer were assumed to be the same as the Sb-doped n-type BaSi_2 film [5]. Figs. 6(b) and 6(c) show the calculated resistance values of BaSi_2 layer (R_{BS})

Figure 6: (a) Schematic illustration of parallel conduction through the BaSi₂ and Si layers, and a calculated band diagram of a 400 nm film with the electron density (n_{BS}) of $1.0 \times 10^{17} \text{ cm}^{-3}$ in the film. (b) Resistance of the BaSi₂ layer (R_{BS}) calculated from the band alignment as a function of n_{BS} , together with the experimental values for the As-doped samples with a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$. (c) The ratio of R_{BS} to the calculated resistance of the Si layer (R_{Si}).

together with experimental values and the ratio of R_{BS} to the resistance of Si layer (R_{Si}), respectively. R_{BS} is found to decrease with increasing n_{BS} . The experimental R_{BS} values agree well with the calculated ones, indicating that the present assumption and calculation are realistic. The resistance ratio ($R_{\text{BS}}/R_{\text{Si}}$) also decreases with n_{BS} , as seen in Fig. 6(c), which means that conduction through the BaSi_2 layer becomes dominant with increasing n_{BS} . When n_{BS} is smaller than $2 \times 10^{17} \text{ cm}^{-3}$, R_{BS} is larger than R_{Si} , and hence, conduction through the Si layer is preferred. When the As dose is 1.0×10^{13} and $1.0 \times 10^{14} \text{ cm}^{-2}$, most of current possibly flowed through Si. With these doses, therefore, n_{BS} is probably smaller than $2 \times 10^{17} \text{ cm}^{-3}$, corresponding to the activation ratio of 8 % for a dose of $1.0 \times 10^{14} \text{ cm}^{-2}$. In conclusion, it is probably difficult to realize electron density higher than $2 \times 10^{17} \text{ cm}^{-3}$ by As doping without inducing the structural change. When the As dose is as high as $1.0 \times 10^{15} \text{ cm}^{-2}$, high electron density up to an average density of $6.0 \times 10^{19} \text{ cm}^{-3}$ is realized through the formation of the altered layer. The altered layer may be useful for an emitter layer of abrupt pn junctions because a high-electron-density layer can be formed around the surface via the structural change. The structural change would, however, also change the fundamental properties such as band gap of the film. For practical applications, structural and electronic properties of the altered layer should be further explored in future studies.

4. Conclusion

We have studied the As doping of BaSi_2 epitaxial films by means of ion implantation and thermal annealing. It has been found that an altered layer

containing As and O is formed at the surface after annealing at 500 °C when the As dose is as high as $1.0 \times 10^{15} \text{ cm}^{-2}$. This altered layer possibly contributes to electron generation and average electron density up to $6.0 \times 10^{19} \text{ cm}^{-3}$ has been realized. On the other hand, with smaller As doses of 1.0×10^{13} and $1.0 \times 10^{14} \text{ cm}^{-2}$, no altered layer is formed. Without the altered layer, possible highest electron density with annealing at 500 °C is less than $2 \times 10^{17} \text{ cm}^{-3}$, corresponding to the activation ratio of 8 %.

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