N-Type Doping of BaSi₂ Epitaxial Films by Phosphorus Ion Implantation and Thermal Annealing

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Abstract

Phosphorus doping by P implantation and thermal annealing of the BaSi₂ epitaxial film grown on the Si(111) substrate has been studied. Raman spectroscopy results show that the structural damage due to P implantation can be almost removed by annealing within 30 and 1 s at 500 and 700 °C, respectively. The depth profile of P is investigated by secondary ion mass spectroscopy, which reveals considerably slower diffusion kinetics of P at 500 °C than 700 °C. The activation energy of the diffusion is roughly estimated to be 2 eV from the temperature dependence. The Hall measurement of the P-doped films clarifies that the P impurity is an electron donor in BaSi₂. The average electron density up to the order of 10¹⁸ cm⁻³ is observed.

Keywords: Silicide semiconductor, Epitaxial film, Phosphorus impurity,

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1. Introduction

Orthorhombic BaSi₂ is attracting much attention as 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 the photon energy of 1.5 eV [1]. The abundance of the constituent elements in earth's crust is also preferable from the viewpoint of large-scale production. In addition, well-crystalline *a*-axis-oriented films can be grown on either Si(111) or Si(100) substrate [2, 3]. High photoresponsivity corresponding to the internal quantum efficiency exceeding 70% has actually been observed in the epitaxial film grown on the p-type Si(111) substrate having the n⁺-type BaSi₂/p⁺-type Si tunnel junction between them [4].

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]. The electrical properties of BaSi₂ doped with other V-group elements, however, have not been investigated so far. Among them, phosphorus (P) has a similar atomic radius to Si, which may be advantageous for doping with less strain. We have previously revealed the damage recovery and surface/interface segregation of P in BaSi₂ epitaxial films at 600–800 °C within 30 s after P implantation [6]. The P segregation into the BaSi₂/Si interface impeded the electrical characterization of the P-doped films. For the effective doping of P and electrical characterization, the optimization of the annealing condition is necessary. In

the present paper, therefore, we have studied the ion implantation doping of P into the BaSi₂ epitaxial film with various annealing conditions and have revealed the electrical properties of the P-doped BaSi₂ film with suppressed P segregation.

2. Experimental methods

An *a*-axis-oriented 410-nm-thick BaSi₂ film was grown on the p-type Si(111) substrate (1000–10000 Ω·cm in resistivity) by reactive deposition epitaxy (RDE; Ba deposition on hot Si [7]) followed by molecular beam epitaxy (MBE; co-deposition of Ba and Si [2]). An ion-pumped MBE system equipped with a standard Knudsen cell for Ba and an electron-beam evaporation source for Si was used. The BaSi₂ epitaxial film was implanted with P⁺ ions at room temperature at an energy of 35 keV with doses of 1.0×10^{14} and 1.0×10^{15} cm⁻², which correspond to average P densities of 2.4×10^{18} and 2.4×10^{19} cm⁻³, respectively. P-implanted films were subsequently subjected to flash lamp annealing (MILA-5000, ULVAC) at 500 and 700 °C for 30–480 and 1–120 s, respectively, 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 ($\lambda = 488$ nm), 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 prepared on the BaSi₂ surface by radio-frequency magnetron sputtering at room temperature.

Figure 1: Effects of P implantation with a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$ and subsequent annealing at 500 and 700 °C on the Raman spectrum of BaSi₂.

3. Results and discussion

Figure 1 shows the Raman spectra after P implantation and subsequent annealing. All peaks from the as-grown film are attributed to the vibration of discrete $[\text{Si}_4]^{4-}$ tetrahedral anions in the BaSi₂ structure [8]. After P implantation, these peaks become broader, and finally become invisible with a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$. This result agrees well with our previous report [6]. Considering that the penetration depth of the laser is 23 nm [1], the disappearance of the Raman peaks is probably because of the partial destruction of the BaSi₂ crystal structure by P implantation.

As evidenced by sharp peaks after annealing in Fig. 1, this implantation

Figure 2: FWHM values of the A_1 Raman peak after P implantation of $1.0 \times 10^{15} \text{ cm}^{-2}$ and subsequent annealing.

damage can be recovered at 500 and 700 °C. The full-width at half-maximum (FWHM) of the A_1 vibration peak is shown in Fig. 2 as an indicator of the structural damage. The mean values from different points on the film surface are shown with the standard deviation. It is found that the FWHM values are similar to the as-grown level under all the annealing conditions studied. Within 1 s, the damage can be removed almost totally at 700 °C. Also at 500 °C, the damage is almost removed with the annealing duration of 30 s and more. The FWHM values after annealing at 500 °C for less than 480 s are, however, slightly higher than the as-grown level, suggesting that a small amount of damage may remain in these films.

Figure 3 shows the SIMS depth profiles of ^{31}P and ^{138}Ba after P implantation of $1.0 \times 10^{15} \text{ cm}^{-2}$ and subsequent annealing. The region with high ^{138}Ba intensities corresponds to the BaSi_2 layer. The original horizontal axis

Figure 3: SIMS depth profiles of ^{31}P and ^{138}Ba in the as-implemented and annealed samples. P dose is $1.0 \times 10^{15} \text{ cm}^{-2}$.

of sputtering time was converted linearly to the depth, using this BaSi₂ layer thickness. Although the ¹³⁸Ba intensity declines gradually at the interface with the width of approximately 100 nm, this does not mean that some amount of Ba diffused into the substrate. As previously observed by cross-sectional transmission electron microscopy [9], the interface between BaSi₂ and Si is probably abrupt, which is also consistent with the phase diagram showing that BaSi₂ and Si coexist at equilibrium [10]. Instead, the gradual decline of ¹³⁸Ba is possibly due to the limited depth resolution of the present measurements.

The depth profile of the as-implanted sample shows that the implanted P atoms are mostly within the BaSi₂ layer with the peak at 49 nm from the surface. After annealing at 500 °C for 30 s, P atoms migrate slightly from the implanted depth, which is in contrast with previously observed interface segregation within 30 s at 600–800 °C in 100-nm-thick samples [6]. After 480 s at 500 °C, P atoms reach the BaSi₂/Si interface and a small amount of segregation is observed at the interface as well as the surface. At 700 °C, in contrast, the P depth profile similar to the annealing at 500 °C for 480 s is realized after 1 s. And, after 5 s of annealing, the interface segregation is observed. The segregated amount increases with increasing the annealing duration to 120 s. Although it seems that the P atoms diffuse into the Si substrate concurrently with interface segregation, this may not be the case. Since the declining slope of ³¹P in the substrate region is similar to ¹³⁸Ba and the BaSi₂/Si interface is abrupt, the observed ³¹P intensity in the substrate region is possibly due to the limited depth resolution of the present measurements.

From the SIMS depth profiles, the activation energy of P diffusion in BaSi₂ was estimated. Since the depth profile of P after annealing at 500 °C for 480 s is similar to after 1 s at 700 °C, the diffusion length ($\sqrt{D\tau}$) is approximately same between these conditions, where D and τ are the diffusion coefficient and diffusion time, respectively. D is proportional to $\exp(-Q/kT)$, where Q is the activation energy, k the Boltzmann constant, and T temperature. Assuming that the prefactor and the diffusion path do not depend on the annealing temperature, Q can be estimated from the agreement of the diffusion length. The estimated Q value is 2 eV. This Q value is larger than that of either lattice or grain boundary diffusion of Al in BaSi₂ (0.63 and 0.58 eV for lattice and grain boundary diffusions, respectively [11]) while it is smaller than that of B in BaSi₂ (4.6 and 4.4 eV for lattice and grain boundary, respectively [11, 12]). The activation energy of impurity diffusion is influenced by the strain induced by the impurity incorporation to the lattice [13]. Group III and V impurities in BaSi₂ are considered to substitute for Si [14, 15]. While the covalent radii of Al (1.21 Å) and P (1.07 Å) are similar to that of Si (1.11 Å), that of B (0.84 Å) is smaller by 24 % [16], which would lead to larger local strain around B. Large activation energy of B diffusion is therefore consistent with the strain effect. On the other hand, the smaller activation energy of Al diffusion than P does not seem to be explained in terms of strain. Many possible reasons are conceivable such as the diffusion path and the bonding characteristics, which need to be examined in future studies to determine the origin of activation energy.

The electrical properties were investigated by the van der Pauw method. With annealing durations of 1 and 5 s at 700 °C, the Hall effect was not

Figure 4: Calculated band diagrams of n-type BaSi₂/p-type Si structures with various electron density (n) in BaSi₂. E_C , E_V , and E_F are conduction band minimum, valence band maximum, and the Fermi level, respectively.

detected with the voltage detection limit of the order of 10 μ V and the magnetic field of up to 0.37 T. This is possibly because the annealing durations are so short that negligible P atoms are activated, and as a result, there are both n- and p-type regions in these samples. Figure 4 shows the band diagrams of studied sample structures, numerically calculated by the Poisson equation under the charge neutral condition. Since the electron affinity of BaSi₂ is smaller by 0.8 eV than Si [17], electron migration from n-type BaSi₂ into p-type Si occurs upon the fabrication of contact, which produces p-type region in BaSi₂. At the same time, an n-type region appears in Si. When the electron density is as small as the undoped film ($5 \times 10^{15} \text{ cm}^{-3}$ [18]), the thickness of the p-type BaSi₂ region is of the order of 100 nm. Thus, the sample structure should be regarded as a layered structure of n-type

Figure 5: Area electron density and that averaged by the film thickness in the P-doped samples as a function of annealing conditions.

BaSi₂/p-type BaSi₂/n-type Si/p-type Si. Although the n- and p-type layers of BaSi₂ are separated by a depletion layer, the grain boundaries, which are normal to the substrate surface [12], may act as a leakage path. During the Hall measurement, therefore, current flowed in both n- and p-type layers, which would be the reason that Hall voltages were not detected.

With increasing the annealing duration more than 5 s at both 500 and 700 °C, the Hall effect was observed, and the majority carriers were determined to be electrons. Figure 5 shows the area electron density and that averaged by the BaSi₂ film thickness determined by the van der Pauw method. By annealing at 500 °C, the electron density increases with annealing duration and P dose, indicating that the P impurity is an electron donor in BaSi₂ and the activation ratio increases with annealing duration. The maximum area electron density achieved is $9.0 \times 10^{13} \text{ cm}^{-2}$ after annealing at 500 °C for 480 s, corresponding to the activation ratio of 9.0 %. This is consistent with

the band diagrams in Fig. 4, which shows that the p-type region thickness decreases with the increase of electron density in BaSi₂.

When annealed at 700 °C, the electron density is smaller than 500 °C. Annealing at this temperature is, therefore, not efficient for the activation of P impurity. In addition, with annealing duration, the electron density slightly decreased, suggesting that P impurity becomes inactive by surface or interface segregation.

To investigate the current path during the Hall measurement, the BaSi₂ film was partly etched so that current cannot flow through the BaSi₂ layer but flow through Si during the Hall measurement. The results are also shown in Fig. 5. It is found that the electron density decreases after etching. This is clear evidence that current flows through both the BaSi₂ and Si layers before etching. Since the most of P atoms are located in the BaSi₂ layer, as shown in Fig. 3, it can be concluded that the P impurity is an electron donor in BaSi₂. The difference in the area electron density between before and after etching is up to $7.8 \times 10^{13} \text{ cm}^{-2}$, which indicates that the area electron density of the order of 10^{13} – 10^{14} cm^{-2} can be achieved by P doping, corresponding to the average volume electron density of the order of 10^{18} cm^{-3} .

4. Conclusion

We have studied the P doping of the BaSi₂ epitaxial film by means of ion implantation and thermal annealing. It has been found that the irradiation damage can be almost removed by annealing within 30 and 1 s at 500 and 700 °C, respectively. SIMS results have revealed that the P diffusion during annealing at 500 °C is considerably slower than at 700 °C. The activation

energy of diffusion, estimated from the temperature dependence of the depth profile of P, is 2 eV. It has been clarified by the Hall measurement that the P impurity is an electron donor in BaSi₂. The electron density of the order of 10^{18} cm^{-3} can be achieved by P doping.

Acknowledgments

A part of this work was supported by “Center for Fusion Research of Nano-Interface Devices, Tohoku University” of “Low-Carbon Research Network” funded by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. This work was also supported by CREST of the Japan Science and Technology Agency.

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