Structural and electrical characterization of crack-free BaSi₂ thin films fabricated by thermal evaporation

Kosuke O. Hara^{a,b,*}, Junji Yamanaka^a, Keisuke Arimoto^a, Kiyokazu Nakagawa^a, Takashi Suemasu^{b,c}, Noritaka Usami^{b,d}

^aCenter for Crystal Science and Technology, University of Yamanashi, 7-32 Miyamae, Kofu, Yamanashi 400-8511, Japan

^bCore Research for Evolutional Science and Technology, Japan Science and Technology Agency, Gobancho, Chiyoda, Tokyo 102-0076, Japan

^cInstitute of Applied Physics, University of Tsukuba, 1-1-1 Tennohdai, Tsukuba, Ibaraki 305-8573, Japan

^dGraduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Abstract

The BaSi₂ semiconductor is a promising candidate for an earth-abundant solar cell absorber. In this study, we have realized a crack-free BaSi₂ film by a simple **thermal** evaporation technique on a CaF₂ substrate at a growth temperature of 500 °C for electrical characterization. A Si layer preliminarily formed on the substrate by sputtering is a key to obtain stoichiometric BaSi₂ film. Detailed structural characterization of the evaporated films with different Si layer thicknesses by X-ray diffraction, scanning and transmission electron microscopy demonstrates that a crack-free 370-nm-thick BaSi₂ film is formed by consuming the Si layer. It is observed that the 90-nm-thick bottom part is microcrystalline and contains Ar atoms, which come from Si deposition atmosphere. The surface of the BaSi₂ layer is found to be

*Corresponding author. Tel +81-55-220-8614; fax: +81-55-254-3035
Email address: khara@yamanashi.ac.jp (Kosuke O. Hara)

covered by an amorphous Si layer due to Si-rich vapor at the last stage of evaporation. Electrical properties of the BaSi₂ film is revealed by Hall measurement and the electron density and mobility are found to be $6 \times 10^{20} \text{ cm}^{-3}$ and $0.04 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively. Owing to a better crystalline quality contributed by the preliminarily-deposited Si layer, minority-carrier lifetime of the evaporated film ($0.6 \text{ }\mu\text{s}$) is twenty times longer than previous films on glass substrates.

Keywords: Barium silicide, Silicide semiconductor, Physical vapor deposition, Electrical property, Minority carrier lifetime

1. Introduction

In order to considerably suppress greenhouse gas emission by large-scale deployment of photovoltaic technology, high-efficiency solar cells with earth-abundant elements are necessary. Orthorhombic BaSi₂ is attracting much attention as a light absorbing material because of an appropriate indirect absorption edge (1.13–1.34 eV [1–3]) for single-junction solar cells and high optical absorption coefficients, reaching $3 \times 10^4 \text{ cm}^{-1}$ for a photon energy of 1.5 eV [3]. The abundance of constituent elements in the earth’s crust is also preferable for large-scale production. The potential of this material for high efficiency devices has been demonstrated by long minority-carrier lifetime and diffusion length up to $11 \text{ }\mu\text{s}$ [4] and approximately $10 \text{ }\mu\text{m}$ [5], respectively.

BaSi₂ films can be grown by the molecular beam epitaxy (MBE) [6, 7], radio-frequency sputtering [8, 9], and vacuum evaporation techniques [10, 11]. The MBE enables high-quality *a*-axis-oriented films on Si(111) and Si(100)

substrates [6, 7]. The long carrier lifetime and diffusion length mentioned above were measured on the epitaxial films. The sputtering deposition, which was developed for large-area and high-speed growth, realized one- μm -thick polycrystalline films with optical properties comparable to the epitaxial film [9]. The evaporation technique is a simpler deposition method than the others. An air-stable BaSi_2 source can be used without any pretreatment, while the MBE uses a reactive Ba source and the sputtering method requires compacting the powder to make a target. It should also be noted that the deposition rate (300 nm/min) of the evaporation method is considerably higher than sputtering (30 nm/min [9]) and MBE (2 nm/min [12]).

Single-phase BaSi_2 films have been realized on Si and glass substrates at 500–600 °C by **thermal** evaporation [10, 11], and it has been revealed that the evaporated films have suitable optical properties and carrier lifetime for thin-film solar cell applications [10]. We have also investigated the film growth mechanism and found that the vapor composition changes from Ba rich to Si rich during evaporation and is Ba rich on average. A high growth temperature is needed to eliminate the composition gradient and Ba rich part through diffusion [10, 11]. Electrical properties, however, are still unknown due to cracking of the films on insulating glass substrates. The cracking is probably due to the mismatch of thermal expansion coefficients between BaSi_2 and glass substrates [10]. In this study, therefore, we have employed a CaF_2 substrate, which has a similar linear expansion coefficient ($19\text{--}20 \times 10^{-6} \text{ K}^{-1}$ [13, 14]) to BaSi_2 ($17.4, 14.9, \text{ and } 14.8 \times 10^{-6} \text{ K}^{-1}$ along the a , b , and c axes, respectively [15]). Since the vapor produced from the BaSi_2 source is Ba-rich in composition [10], Si atoms must be additionally supplied for the

formation of stoichiometric BaSi_2 . We therefore introduce a Si supply layer on the CaF_2 substrate. The purpose of the present study is to realize a crack-free BaSi_2 evaporated film, which is essential for electrical characterizations. It is demonstrated that the use of CaF_2 substrate is effective for preventing cracks and that the difference in the linear expansion coefficient is the primary cause of crack formation. The effects of the preliminarily-deposited Si layer on the crystalline quality of evaporated films are also discussed.

2. Experimental method

A Si layer was prepared by radio-frequency magnetron sputtering on a single-crystalline CaF_2 substrate (orientation not specified) at room temperature. We call this layer a Si supply layer hereafter. Commercial BaSi_2 source (99% in purity, Kojundo Chemical Lab.) was melted on a tungsten boat and the vapor was deposited on the CaF_2 substrates with Si supply layers heated at 500 °C. The main metallic impurities in the BaSi_2 source are Sr (0.5%), Ca (0.4%), and Al (0.01%). The Si supply layer is amorphous at both room temperature and 500 °C, which was confirmed by broad Raman bands peaked at 467–468 cm^{-1} (not shown). The details of the evaporation procedure are mentioned in our previous papers [10, 11]. While fixing the evaporation amount, the effects of different initial Si thicknesses (t_{Si}) of 0, 129, and 230 nm were studied. The structure of films was characterized by grazing-incidence X-ray diffraction analysis (XRD, Bruker Discover D8) with Cu $K\alpha$ radiation, scanning electron microscopy (SEM, JEOL JSM-7001FA), and transmission electron microscopy (TEM, FEI Tecnai Osiris). The physical properties of films were investigated by Hall measurement (TOYO ResiTest8308) with the

van der Pauw method and microwave-detected photoconductivity decay (μ -PCD, KOBELCO LTA-1512EP) measurement. For Hall measurement, Al ohmic contacts were deposited on the surface by radio-frequency magnetron sputtering at room temperature. The excitation source of μ -PCD was a 5 ns laser pulse with a wavelength of 349 nm. The BaSi₂ source was also analyzed by powder XRD (Rigaku MultiFlex).

3. Results and discussion

Figure 1 shows XRD patterns of the evaporated films. All peaks can be indexed to the orthorhombic BaSi₂ phase, indicating that the crystalline phase is only BaSi₂. Without a Si supply layer [Fig. 1(a)], however, the peak intensity is low and only three peaks are clearly observed. This is possibly because Ba-rich film without a Si layer reacted with air to form Ba oxide upon air exposure, leading to smaller BaSi₂ volume than the films with Si supply layers. With $t_{\text{Si}} = 129$ nm [Fig. 1(b)], several peaks show higher intensities than the theoretical pattern, while similar relative intensities to the theoretical pattern are observed for $t_{\text{Si}} = 230$ nm [Fig. 1(c)]. This result indicates that BaSi₂ film with $t_{\text{Si}} = 129$ nm has preferred orientation while that with 230 nm is randomly oriented. The diffraction indices are displayed in the figure for significantly stronger peaks than the theoretical one. Since $h0l$ ($h > l$) peaks are noticeable, the BaSi₂ crystals may be oriented around the a and c axes with $t_{\text{Si}} = 129$ nm. This preferred orientation is probably not due to the epitaxy on the CaF₂ substrate because a thin Si layer remained between BaSi₂ and CaF₂ substrate, as found from the TEM images shown later in Fig. 3. The templating effect of the Si supply layer is also not

Figure 1: XRD patterns of the evaporated films with (a) $t_{\text{Si}} = 0$, (b) 129, and (c) 230 nm. The X-ray incidence angle is 3.8° . Powder XRD pattern of the BaSi₂ source and a theoretical 2θ - θ pattern of randomly-oriented orthorhombic BaSi₂ phase are also displayed below the thin-film patterns.

Figure 2: (a)–(c) Cross-section and (d)–(f) plan-view SEM images of the evaporated films with (a, d) $t_{\text{Si}} = 0$, (b, e) 129, and (c, f) 230 nm.

likely since the Si supply layer was amorphous, which was confirmed by Raman spectroscopy from both the front and rear surfaces after annealing at 500 °C for 4.5 h in the evaporation chamber without BaSi₂ evaporation. Although the reason of the preferred orientation is not clear, the films without crystalline impurities are formed with the present method.

The cross-section and plan-view SEM images of the evaporated films are shown in Fig. 2. Without a Si layer, the interface between the film and substrate is rough [Fig. 2(a)], suggesting that the film reacted with the substrate. On the other hand, with Si layers, flat interfaces are observed. In particular, for $t_{\text{Si}} = 230$ nm, there is a 97-nm-thick dark layer exactly on the substrate. This dark layer is presumably a residual Si supply layer. That is, $230 - 97 = 133$ nm of Si was consumed during the growth of 422 nm BaSi₂. A t_{Si} value of 129 nm was decided from this Si consumption rate so that the

Si supply layer can be totally consumed. Such a dark layer, therefore, is not observed in Fig. 2(b).

The plan-view SEM images [Figs. 2(d)–(f)] show no cracks on the films. This is in contrast with previous cracked films on alkali-free glass substrates [10]. On alkali-free glass substrates, approximately ten cracks were found in the area of $13 \times 23 \mu\text{m}^2$ [10], while no cracks were found in the same area size of the present films. Even at higher magnification [Figs. 2(d)–(f)], cracks are not observed. Linear expansion coefficient of the alkali-free glass ($3.55 \times 10^{-6} \text{ K}^{-1}$) is 4.17–4.90 times smaller than BaSi_2 (17.4, 14.9, and $14.8 \times 10^{-6} \text{ K}^{-1}$ along the a , b , and c axes, respectively [15]), while that of CaF_2 is only 1.09–1.35 times larger than BaSi_2 [13, 14]. Present results have demonstrated that matching of linear expansion coefficients is important to fabricate crack-free BaSi_2 evaporated films.

The Si/Ba molar ratios determined by energy-dispersive X-ray spectroscopy (EDX) with an acceleration voltage of 15 kV are 1.28 and 2.38 for $t_{\text{Si}} = 0$ and 129 nm, respectively. Without a Si supply layer, amorphous or microcrystalline Ba compounds such as oxide possibly coexist with BaSi_2 , which may be the reason for the Si/Ba ratio lower than 2. With $t_{\text{Si}} = 129 \text{ nm}$, the Si/Ba ratio is higher than 2, in spite of total consumption of the Si supply layer. This is presumably because of a surface Si layer, as shown below by TEM observation. The variation of Si/Ba ratio clearly shows the usefulness of a Si supply layer for preparing stoichiometric BaSi_2 films.

For more detailed microstructural characterization, the evaporated film with $t_{\text{Si}} = 129 \text{ nm}$ was subjected to TEM analysis. Fig. 3(a) shows a bright-field image of the cross section. The film consists of three layers. The top

Figure 3: Cross-section TEM analysis results of the evaporated film with $t_{\text{Si}} = 129$ nm.
(a) Bright-field image, (b) High resolution image, (c) HAADF image and EDX maps.

layer is thinnest (40 nm) and uniform along the surface. The Fourier transform of a high resolution image [Fig. 3(b)] shows it is amorphous. The second layer is thickest (280 nm) and consists of grains elongated toward the growth direction. The grain size is more than 100 nm along the growth direction while it is several tens of nm along an in-plane direction. The third layer (90 nm thick) directly on the substrate seems to consist of smaller grains than the second layer. This layer may have originally been the Si layer.

To investigate the elemental distribution, EDX maps were acquired together with a high-angle annular dark field (HAADF) image. As can be observed in the HAADF image of Fig. 3(c), the elemental distribution varies with layers. It is observed from the Ba $K\alpha$ and Si $K\alpha$ maps that Ba and Si atoms distribute uniformly in the second layer, indicating that the thickest layer consists of $BaSi_2$. Si $K\alpha$ signal is strong also from the top layer and the film-substrate interface. Since another signal is not significantly detected from the top layer, the top layer is concluded to be amorphous Si. This amorphous Si layer was probably formed at the last stage of film growth since the vapor composition changes from Ba rich to Si rich during evaporation [11]. The interface Si is presumably the residue of the Si supply layer. In the bottom layer, together with Ba and Si, Ar was detected. These Ar atoms are probably from the flowing gas during sputtering. Since Ar is inert, the bottom layer is presumably $BaSi_2$ with Ar inclusion. The Ca $K\alpha$ and F $K\alpha$ maps show that no detectable diffusion of Ca and F occurs from the substrate. A significant part (second and third layers of totally 370 nm) of the evaporated film therefore consists of $BaSi_2$. To fabricate a uniform $BaSi_2$ layer up to the top surface, the $BaSi_2$ evaporation amount should be

controlled.

Electrical properties of the evaporated films were investigated by Hall measurement with the van der Pauw method. Only the film with $t_{\text{Si}} = 129$ nm could be totally characterized because the Al contacts were not ohmic for $t_{\text{Si}} = 0$ nm, and because Hall voltage was not observed for $t_{\text{Si}} = 230$ nm. The evaporated film with $t_{\text{Si}} = 129$ nm exhibited n-type conductivity. Its electron density (n) is $6 \times 10^{20} \text{ cm}^{-3}$ and Hall mobility (μ) is $0.04 \text{ cm}^2/\text{V}\cdot\text{s}$, which are high and low as a semiconductor film, respectively. This result was probably affected by the surface amorphous Si layer through two possible mechanisms. One possibility is that we measured the amorphous Si film. This is, however, unlikely because an amorphous Si layer without the termination of dangling bonds is generally difficult to be doped. **In addition, for reference, the amorphous Si supply layer formed by sputtering has an appreciably larger resistivity of $3.0 \times 10^3 \Omega\cdot\text{cm}$ than the BaSi_2 film ($0.29 \Omega\cdot\text{cm}$), supporting that current flow mainly through the surface amorphous Si layer is not probable.** Another possible effect is the underestimation of Hall voltage due to voltage drop in the amorphous layer. The n and μ values may, therefore, have been overestimated and underestimated, respectively.

The revealed n and μ values of the as-grown BaSi_2 film are four orders of magnitude higher and lower than an epitaxial film, respectively [16, 17]. Since such a high n value brings about Auger recombination and a low μ value leads to short carrier diffusion length, the as-grown film is not suitable for an absorption layer of solar cells. **Impurities in the BaSi_2 source (mainly Sr 0.5%, Ca 0.4%, and Al 0.01%) may be one reason of high n . The Sr and Ca impurities would, however, not significantly affect n because they belong**

to the same alkaline-earth metal group as Ba. In fact, it is reported that Sr-substituted BaSi₂ remains semiconducting up to 50 % substitution with a band gap of 1.1–1.4 eV [18–20]. The Al impurity is known to work as acceptor in BaSi₂. It is reported that the hole concentration is limited to 10¹⁷ cm⁻³, and the Al atoms diffuse out from BaSi₂ during high temperature annealing [21, 22]. These impurities, therefore, cannot account for the high electron density in the evaporated film. Another possible factor of high n and low μ values is the crystal defects formed due to high-rate deposition. Since our previous studies show that crystal defects such as implantation damage can be removed within 30 s at 600–800 °C [23, 24], thermal annealing at 600–800 °C may reduce the defects, leading to the decrease in n and increase in μ . Growth condition such as growth temperature may similarly affect electrical properties. Investigation is now in progress on the relationship between electrical properties and the conditions of growth and post annealing.

To investigate the effects of the Si supply layer on crystalline quality, minority-carrier lifetime (τ) was evaluated by the μ -PCD method. Figure 4 shows the μ -PCD curve of the evaporated film with $t_{\text{Si}} = 129$ nm. In accordance with epitaxial films [25], three-stage decay was observed. The first decay is possibly due to Auger recombination with high excess carrier density and recombination in the surface amorphous Si layer. The second decay would correspond to Shockley–Read–Hall recombination in the BaSi₂ layer. The third decay is presumably caused by the carrier trapping effect. From the second decay, τ is 0.6 μ s. This τ value is twenty times higher than those in the BaSi₂ evaporated films grown on alkali-free glass substrates without Si supply layers [10]. This enhancement of τ is probably because the Si supply

Figure 4: The μ -PCD curve of the evaporated film with $t_{\text{Si}} = 129$ nm.

layer contributes to the growth of BaSi_2 with fewer defects. On the alkali-free glass without a Si supply layer, Si atoms are supplied to the growth of BaSi_2 from the substrate through a reaction of $5\text{Ba} + 2\text{SiO}_2 = 4\text{BaO} + \text{BaSi}_2$ [10]. Here, the BaO by-product around the film–substrate interface possibly acts as a diffusion barrier, and impedes the Si supply. Produced films accordingly contain many defects such as Si vacancies. With a Si supply layer, on the other hand, there are no such obstacles. A better crystalline film is therefore produced with a Si supply layer. This is evidenced by sharper XRD peaks with a Si supply layer. The full width at half-maximum of the 112 diffraction peak ($2\theta = 22.6^\circ$) from the film with $t_{\text{Si}} = 129$ nm is 0.27° in Fig. 1(b), while it is 0.47° for the film grown on an alkali-free glass substrate without a Si supply layer [Fig. 1(b) in Ref. 10]. The crystallite size estimated by the Scherrer equation, neglecting microstrain, is 29 nm, larger than the

film on the alkali-free glass without a Si supply layer (17 nm). The surface amorphous Si layer may also contribute to high τ value through surface passivation. For reference, carrier lifetime in the amorphous Si supply layer was unmeasurably small, supporting that the recombination in the surface amorphous Si layer did not contribute to the long carrier lifetime. Assuming that the minority-carrier mobility accords with the majority-carrier mobility determined by the Hall measurement, the minority-carrier diffusion length can be estimated to be 0.2 μm . Within 0.2 μm , 30 % of the incident light is absorbed for a photon energy of 1.5 eV (absorption coefficient is $2 \times 10^4 \text{ cm}^{-1}$ [10]). For high-efficiency solar cells using BaSi_2 evaporated films, minority-carrier lifetime and mobility should be improved by modifying the growth condition in future studies.

For solar cell applications of BaSi_2 films, overlayers are necessary such as p-type, window, or transparent conducting layers. A crack-free film is a prerequisite to realize such layered structures. Although the film quality should be significantly improved, the present growth method using a substrate with similar thermal expansion coefficient to BaSi_2 and a Si supply layer will be a key technology for devices using BaSi_2 evaporated films.

4. Conclusion

We have realized a crack-free 370-nm-thick BaSi_2 film by thermal evaporation on a CaF_2 substrate with a sputtered Si layer at a growth temperature of 500 °C. The bottom part of the film is microcrystalline and contains Ar inclusions, which is evidence of the consumption of the Si supply layer. The surface of BaSi_2 film is covered by an amorphous Si layer, due to Si-rich vapor

at the last stage of evaporation. n and μ of the BaSi₂ film are $6 \times 10^{20} \text{ cm}^{-3}$ and $0.04 \text{ cm}^2/\text{V}\cdot\text{s}$, respectively. Minority-carrier lifetime ($0.6 \text{ }\mu\text{s}$) is twenty times longer than previous BaSi₂ films on glass substrates because a better crystalline film is obtained owing to a Si supply layer.

Acknowledgments

This work was supported by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency. Authors thank Prof. Onojima, Dr. Nagao, and Ms. Yamamoto of the Univ. of Yamanashi for their help with Hall measurement, powder XRD, and TEM analysis, respectively.

References

- [1] T. Nakamura, T. Suemasu, K. Takakura, F. Hasegawa, A. Wakahara, M. Imai, Investigation of the energy band structure of orthorhombic BaSi₂ by optical and electrical measurements and theoretical calculations, Appl. Phys. Lett. 81 (2002) 1032–1034.
- [2] S. Kishino, T. Imai, T. Iida, Y. Nakaishi, M. Shinada, Y. Takanashi, N. Hamada, Electronic and optical properties of bulk crystals of semiconducting orthorhombic BaSi₂ prepared by the vertical Bridgman method, J. Alloys Compd. 428 (2007) 22–27.
- [3] K. Toh, T. Saito, T. Suemasu, Optical absorption properties of BaSi₂ epitaxial films grown on a transparent silicon-on-insulator substrate using molecular beam epitaxy, Jpn. J. Appl. Phys. 50 (2011) 068001.

- [4] K. O. Hara, N. Usami, K. Nakamura, R. Takabe, M. Baba, K. Toko, T. Suemasu, Determination of bulk minority-carrier lifetime in BaSi_2 earth-abundant absorber films by utilizing a drastic enhancement of carrier lifetime by post-growth annealing, *Appl. Phys. Express* 6 (2013) 112302.
- [5] M. Baba, K. Toh, K. Toko, N. Saito, N. Yoshizawa, K. Jiptner, T. Sekiguchi, K. O. Hara, N. Usami, T. Suemasu, Investigation of grain boundaries in BaSi_2 epitaxial films on $\text{Si}(111)$ substrates using transmission electron microscopy and electron-beam-induced current technique, *J. Cryst. Growth* 348 (2012) 75–79.
- [6] Y. Inomata, T. Nakamura, T. Suemasu, F. Hasegawa, Epitaxial growth of semiconducting BaSi_2 films on $\text{Si}(111)$ substrates by molecular beam epitaxy, *Jpn. J. Appl. Phys.* 43 (2004) L478–L481.
- [7] K. Toh, K. O. Hara, N. Usami, N. Saito, N. Yoshizawa, K. Toko, T. Suemasu, Molecular beam epitaxy of BaSi_2 thin films on $\text{Si}(001)$ substrates, *J. Cryst. Growth* 345 (2012) 16–21.
- [8] T. Yoneyama, A. Okada, M. Suzuno, T. Shibutami, K. Matsumaru, N. Saito, N. Yoshizawa, K. Toko, T. Suemasu, Formation of polycrystalline BaSi_2 films by radio-frequency magnetron sputtering for thin-film solar cell applications, *Thin Solid Films* 534 (2013) 116–119.
- [9] N. A. A. Latiff, T. Yoneyama, T. Shibutami, K. Matsumaru, K. Toko, T. Suemasu, Fabrication and characterization of polycrystalline BaSi_2 by RF sputtering, *Phys. Status Solidi C* 10 (2013) 1759–1761.

- [10] K. O. Hara, Y. Nakagawa, T. Suemasu, N. Usami, Realization of single-phase BaSi₂ films by vacuum evaporation with suitable optical properties and carrier lifetime for solar cell applications, Jpn. J. Appl. Phys. 54 (2015) 07JE02.
- [11] Y. Nakagawa, K. O. Hara, T. Suemasu, N. Usami, Fabrication of single-phase polycrystalline BaSi₂ thin films on silicon substrates by vacuum evaporation for solar cell applications, Jpn. J. Appl. Phys., accepted.
- [12] M. Baba, K. Nakamura, W. Du, M. A. Khan, S. Koike, K. Toko, N. Usami, N. Saito, N. Yoshizawa, T. Suemasu, Molecular beam epitaxy of BaSi₂ films with grain size over 4 μ m on Si(111), Jpn. J. Appl. Phys 51 (2012) 098003.
- [13] S. Bedi, M. Singh, J. Singh, Temperature dependence of the second order elastic constants of fluorite solids, Solid State Commun. 85 (1993) 805–809.
- [14] R. J. Angel, The high-pressure, high-temperature equation of state of calcium fluoride, CaF₂, J. Phys.: Condens. Matter 5 (1993) L141.
- [15] M. Imai, Thermal expansion of alkaline-earth-metal disilicides AeSi₂ (Ae = Ca, Sr, and Ba), Jpn. J. Appl. Phys. 50 (2011) 101801.
- [16] K. Morita, Y. Inomata, T. Suemasu, Optical and electrical properties of semiconducting BaSi₂ thin films on Si substrates grown by molecular beam epitaxy, Thin Solid Films 508 (2006) 363–366.
- [17] W. Du, M. Baba, K. Toko, K. O. Hara, K. Watanabe, T. Sekiguchi,

- N. Usami, T. Suemasu, Analysis of the electrical properties of Cr/n-BaSi₂ Schottky junction and n-BaSi₂/p-Si heterojunction diodes for solar cell applications, J. Appl. Phys. 115 (2014) 223701.
- [18] K. Morita, M. Kobayashi, T. Suemasu, Optical Absorption Edge of Ternary Semiconducting Silicide Ba_{1-x}Sr_xSi₂, Jpn. J. Appl. Phys. 45 (2006) L390–L392.
- [19] Y. Imai, A. Watanabe, Energetic and the electronic structural consideration of the 13th Group element (Ga and In) impurity doping to control the conductivity of BaSi₂, Thin Solid Films 515 (2007) 8219–8225.
- [20] M. Imai, A. Sato, T. Kimura, T. Aoyagi, Basic properties of Sr_{1-x}Ba_xSi₂, Thin Solid Films 519 (2011) 8496–8500.
- [21] M. Takeishi, Y. Matsumoto, R. Sasaki, T. Saito, T. Suemasu, Growth of Al-doped p-type BaSi₂ films by molecular beam epitaxy and the effect of high-temperature annealing on their electrical properties, Phys. Procedia 11 (2011) 27–30.
- [22] M. A. Khan, M. Takeishi, Y. Matsumoto, T. Saito, T. Suemasu, Al- and Cu-doped films on Si(111) substrate by molecular beam epitaxy and evaluation of depth profiles of Al and Cu atoms, Phys. Procedia 11 (2011) 11–14.
- [23] K. O. Hara, N. Usami, Y. Hoshi, Y. Shiraki, M. Suzuno, K. Toko, T. Suemasu, Structural study of BF₂ ion implantation and post annealing of BaSi₂ epitaxial films, Jpn. J. Appl. Phys. 50 (2011) 121202.

- [24] K. O. Hara, Y. Hoshi, N. Usami, Y. Shiraki, K. Nakamura, K. Toko, T. Suemasu, Structural study on phosphorus doping of BaSi₂ epitaxial films by ion implantation, *Thin Solid Films* 534 (2013) 470–473.
- [25] K. O. Hara, N. Usami, K. Toh, M. Baba, K. Toko, T. Suemasu, Investigation of the recombination mechanism of excess carriers in undoped BaSi₂ films on silicon, *J. Appl. Phys.* 112 (2012) 083108.