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On the mechanism of $BaSi_2$ thin film formation on Si substrate by vacuum evaporation

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Abstract

We report on the formation mechanism of $BaSi_2$ thin film on Si substrate grown by vacuum evaporation using $BaSi_2$ granules as source materials. Since the vapor flux at the initial stage of evaporation is known to be Ba-rich, Si supply from the substrate is of crucial importance to obtain homogeneous $BaSi_2$ thin film. In fact, low substrate temperature and/or thick film deposition led to formation of rough film with voids, and the oxidation proceeded upon exposure to air. We revealed that appropriate choice of substrate temperature, film thickness, and post-growth *in-situ* annealing can provide enough diffusion of Si and Ba, leading to realization of homogeneous $BaSi_2$ thin film.

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Keywords: barium desiliside, vacuum evaporation;

1. Introduction

Orthorhombic $BaSi_2$ is attractive material as an absorption layer for single junction thin-film solar cells because it has suitable band gap (1.3 eV [1,2]) and large absorption coefficients (3×10^{-4} cm^{-1} at 1.5 eV[1]). Furthermore, both

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of Ba and Si are earth-abundant and suitable for large-scale production. Fundamental studies clarified various promising properties to certify its potential as the absorption layer of thin film solar cells. These include long diffusion length (10 μm [3]), long minority-carrier lifetime (14 μs [4]), wide range control of electron and hole densities [5-7], application of MoO_x hole transport layer to undoped n-type $BaSi_2$ [8], proposal of tin sulfide/$BaSi_2$ heterojunction solar cell to have a similar band diagram of pn homojunction [9], and so on.

The most of these fundamental studies have been done using $BaSi_2$ epitaxial films grown on Si(111) or Si(100) substrates by molecular beam epitaxy [10-12]. As for practical application, development of alternative method to permit realization of large-scale homogeneous $BaSi_2$ thin film is demanded. For this purpose, polycrystalline $BaSi_2$ was fabricated on glass substrate by radio-frequency sputtering [13, 14]. In our previous study, we proposed to utilize vacuum evaporation method, which enables us to fabricate films simply, quickly and stably. In fact, we have shown that single-phase $BaSi_2$ films can be formed on Si(111) substrate [15] and alkali-free glass substrate [16] by this method. In addition, the mechanism of film growth was discussed and we found that the vapor flux is Ba-rich and the supply of Si to the film is important to obtain homogeneous $BaSi_2$. Then, we speculated that high substrate temperature (≥500 ˚C) wound be necessary to fabricate $BaSi_2$ film. However, high substrate temperatures set a limit to choice of the substrate. It would be useful if we could somehow decrease the substrate temperature based on fundamental understanding of formation mechanisms.

In this paper, we report on the impact of the film thickness, substrate temperature and post-growth annealing times on the formation of $BaSi_2$ thin film on Si substrate grown by vacuum evaporation using $BaSi_2$ granules as source materials. These three factors were found to affect the composition in the film, and the oxidation was found to occur if the diffusion of Ba and Si is not enough. We revealed that appropriate choice of substrate temperature, film thickness, and post-growth *in-situ* annealing is necessary to realize homogeneous $BaSi_2$ thin film.

2. Experimental procedure

The films were deposited by vacuum evaporation under heating to form stoichiometric $BaSi_2$ film. 20×20-mm^2 Floating Zone n-type Si (111) (ρ>1000 Ω·cm) wafers were used for substrates after cleaning with 1% HF solution to remove SiO_2 on the surface. $BaSi_2$ (99% in purity, Kojundo Chemical Lab.) granules were used as sources and melted by heating for approximately 2 minute. The film thickness was varied by changing the source weight. The distance between source and substrate was set as 19 cm. The base pressure was lower than 1×10^{-5} mbar.

The grown films were characterized by Raman spectroscopy (Nanofinder, Tokyo Instruments, Inc.) with Ar^+ ion laser (λ= 488 nm), energy dispersive X-ray spectrometry (EDX), and scanning electron microscopy (SEM; JSM-7001FA, JEOL).

3. Results and discussion

Figure 1 shows cross-sectional SEM images of samples deposited under various conditions. Figures 1 (a) and (b) show the film deposited at 600 and 400 ˚C, respectively. Both of the films were fabricated by using the same weight of source. The film deposited at 600 ˚C is dense and the surface is flat. On the other hands, the film deposited at 400

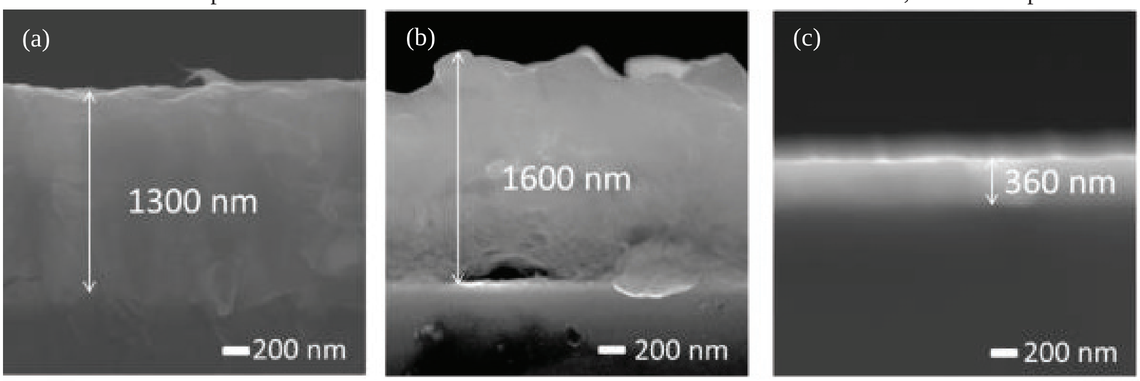

Fig. 1. Cross-sectional SEM images of the film grown at (a) 600 and (b), (c) 600 ˚C.

˚C includes voids and the surface is very rough. Consequently, the film thickness is slightly thicker than that deposited at 600 ˚C. Figure 1 (c) shows the film deposited at 400 ˚C with smaller weight of source compared to the film shown in Fig. 1 (a) and (b). In spite of low growth temperature, the film morphology was improved.

Figure 2 shows Raman spectra of the films with various thicknesses deposited at 400 ˚C. For comparison, Raman spectrum of the 1300 nm thick film deposited at 600 ˚C is also shown. It is seen that all samples show peaks originating from phonons associated with $BaSi_2$ in 200-500 cm^{-1}[17]. Crystalline Si peak at 521 cm^{-1} is seen only in the spectrum of the 1600 nm thick film deposited at 400 ˚C. This result indicates that the film contains crystalline Si. It is probably due to oxidation of the film upon expose to air to produce BaO_x and crystalline Si. Raman spectra of the 630 and 320 nm thick films contain broad peak around 400 to 550 cm^{-1}, which suggests that amorphous Si is included in the films. Formation of amorphous Si would be due to the Si-rich vapor flux at the final stage of evaporation since the most of Ba are consumed at the earlier stage [15]. These results indicate that there is a limitation in the thickness for realization of homogeneous $BaSi_2$ films by vacuum evaporation depending on the substrate temperature, and the critical thickness increases with increasing substrate temperature.

In order to clarify underling mechanisms, we used EDX measurement to compare the film composition. Figure 3 shows the oxygen content defined by the intensity ratio of O $K\alpha$ peak to Ba $L\alpha$ peak as a function of the film thickness. It is seen that the thick film deposited at low substrate temperature includes high amount of oxygen, which suggests that the film was oxidized upon exposure to air. On the other hand, oxidization can be suppressed by decreasing film thickness. This result indicates that homogeneous $BaSi_2$ films can be formed under conditions to permit sufficient diffusion of Ba and Si atoms. From these results, it is considered that film thickness and substrate temperature variation affect the diffusion length, and the diffusion of Ba and Si atom is one of the key factors to fabricate homogeneous $BaSi_2$ film.

To investigate the effect of annealing time to control the diffusion length, we prepared three samples at 400 ˚C. The samples are annealed *in-situ* after deposition in the vacuum chamber. Annealing time was set at 0, 30 and 60 minute. Figure 4 shows effect of annealing on the oxygen ratio and film thickness. It is found that oxidation ratio decrease with increasing annealing times accompanied by decrease of film thickness. This suggests that *in-situ* annealing may suppress oxidation by sufficient diffusion of Ba and Si atoms. However, reevaporation of the films occurs as evidenced by the decrease of film thickness.

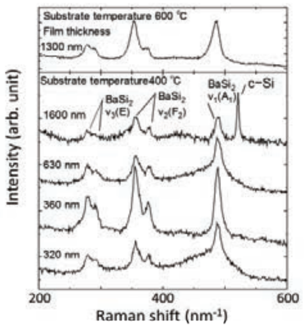

Fig. 2. Raman spectra of the films deposited at 400 and 600 ˚C.

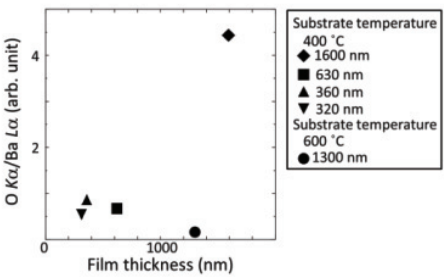

Fig. 3. The effect of film thickness and substrate temperature on oxygen ratio

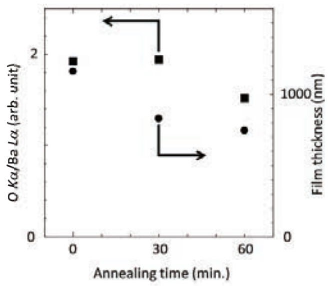

Fig. 4. Oxygen ratios and film thickness plotted against annealing time. Squares and circles show oxygen ratio and film thickness, respectively

From these results, the mechanism of film growth is discussed as follows. Inhomogeneous film composition is eliminated by diffusion assisted by thermal energy. Thus, when the thin films are deposited at low substrate temperature or the thick films are deposited at high substrate temperature, Ba and Si atoms can be diffused enough. However, when the thick films are deposited at low substrate temperature, remaining inhomogeneous part causes the oxidation. Annealing and high substrate temperature may enhance the diffusion distance. Therefore, if we need to fabricate homogeneous $BaSi_2$ films at lower temperature, it is required to reduce the film thickness or increase annealing time.

4. Conclusion

We fabricated the $BaSi_2$ film under various conditions with vacuum evaporation and investigated the effect of substrate temperature, film thickness, and annealing times on the homogeneity of the film. We clarified the formation mechanism of homogeneous $BaSi_2$ films, and diffusion of Ba and Si atoms was found to be important. When we need to fabricate homogeneous $BaSi_2$ at low substrate temperature, thin film thickness or long time anneal is required to permit sufficient diffusion of Ba and Si atoms.

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References

[1] K. Toh, T. Saito, T. Suemasu, Optical absorption properties of $BaSi_2$ epitaxial films grown on a transparent silicon-on-insulator substrate using molecular beam epitaxy, Jpn. J. Appl. Phys. 50, (2011), 068001.

[2] K. Morita, Y. Inomata, T. Suemasu, Optical and electrical properties of semiconducting $BaSi_2$ thin films on Si substrates grown by molecular beam epitaxy,Thin Solid Films 508 (2006) 363.

[3] M. Baba, K. Toh, K. Toko, N. Yoshizawa, K. Jiptner, T. Sekiguchi, K.O. Hara, N. Usami, T. Suemasu, Investigation of grain boundaries in $BaSi_2$ epitaxial films on si(111) substrates using transmission electron microscopy and electron-beam-induced current technique, J. Cryst. Growth 348 (2012) 75.

[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] W. Du, M. Baba, K. Toko, K. O. Hara, K.Watanabe, T. Sekiguchi, N. Usami, T. Sumasu, Analysis of the electrical properies of Cr/n-$BaSi_2$ Schottky iunction and n-$BaSi_2$/p-Si heterojunction diodes for solar cell applications, J. Appl. Phys. 115 (2014) 16

[6] M. A. Khan, K. O. Hara, W. Du, M. Baba, K. Nakamura, M.Suzuno, K.Toko, N. Usami, T. Suemasu, *In-situ* heavily p-type doping of over 10^{20} cm^{-3} in semiconducting $BaSi_2$ thin films for solar cells applications, Appl. Phys. Lett. 102 (2013) 112107

[7] M. Kobayashi, Y. Matumoto, Y. Ichikawa, D. Tsukada, T. Suemasu,Control of Electron and Hole Concentratios in Semiconducting Silicide $BaSi_2$ with Impurities Grown by Molecular Beam Epitaxy, Appl. Phys. Express 1 (2008) 05403

[8] W. Du, R. Takabe, M. Baba, H. Takeuchi, K. O. Hara, N. Usami, T. Suemasu, Formation of $BaSi_2$ heterojunction solar cells using transparent MoOx hole transport layers, Appl. Phys. Lett. 106 (2015) 122104

[9] K. O. Hara, N. Usami, Numerical simulation of new earth-aboundant SnS/$BaSi_2$ thin-film solar cells with high efficiencies exceeding 20 %, 6th World Conference on Photovoltaic Energy Conversion, Kyoto, Japan, November (2014)

[10] R. A. Mckee, F. J. Walker, $BaSi_2$ and thin film alkaline earth silicides on silicon, Appl. Phys. Lett. 63 (1993) 2818

[11] Y. Inomata, T. Nakamura, T. Suemasu, F. Hasegawa, Epitaxial growth of semiconduction BaSi2 films on Si (111) substrate by molecular beam epitaxy, Jpn. J. Appl. Phys. 43 (2004) L771

[12] K. Toh, K. O. Hara, N. Usami, N. Saito, N. Yoshizawa, K. Toko, T. Suemasu, Molecular beam epitaxy of $BaSi_2$ thin films on Si(001) substrates, J. Cryst. Growth 345 (2012) 16

[13] T. Yoneyama, A. Okada, M. Suzuno, T. Shibutami, K Matsumaru, N. Saito, N. Yoshizawa, K. Toko, T.Suemasu, Formation of polycrystalline BaSi2 films by radio-frequency magenetron sputtering for thin-film solar cell applications, Thin Solid Films 534 (2013) 116

[14] N. A. A. Latiff, T. Yoneyama, T. Shibutami, K. Matsumaru, K. Toko, T. Suemasu, Fabrication and characterization of polycrysatalline BaSi2 by RF sputtring, Phys. Status Solidi C (2013) 1

[15] Y. Nakagawa, K. O. Hara, T. Suemasu, N. Usami, Fabrication of single-phase polycrystalline $BaSi_2$ thin films on silicon substrates by vacuum evaporation for solar cell applications, Jpn. J. Appl. Phys. in press.

[16] K. O. Hara, Y. Nakagawa, T. Suemasu, N. Usami, Realization of single-phase $BaSi_2$ films by vacuum evaporation with suitable optical properties and carrier lifetime for solar cell applications, Jpn. J. Appl. Phys. 54 (2015) 07JE02

[17] M. Somer, Vibration spectra of the Cluster Anions$[E_4]^{4-}$ in the metallic sodium and Barium Compounds Na_4E_4 and Ba_2E_4(E=Si,Ge), Z. Anorg. Allg. Chem., 626 (2000) 2478