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Significant improvement of photoresponsivity of polycrystalline $BaSi_2$ films directly formed on heated Si(111) substrates by sputtering

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Abstract

We succeeded in forming approximately 150-nm-thick $BaSi_2$ films on a Si(111) substrate at 600 °C. The reduction in electron concentration ($n = 2 \times 10^{16}$ cm^{-3}) by three orders of magnitude compared to that previously reported ($n = 7 \times 10^{19}$ cm^{-3}) and the resultant photoresponsivity enhancement by 400 times were achieved. The photoresponsivity increased with bias voltage V_{bias} applied between the top and bottom electrodes and reached approximately 0.2 A/W at 1.5 eV at $|V_{bias}| = 0.5$ V, corresponding to *EQE*=40%.

1. Introduction

Barium disilicide ($BaSi_2$) [1,2] has attractive properties for solar cell applications such as a band gap of 1.3 eV [3], a large absorption coefficient (α) of 3×10^4 cm^{-1} at 1.5 eV [3], inactive grain boundaries [4], and a large minority-carrier lifetime ($\tau \sim 10$ μs) [5]. We have achieved efficiencies approaching 10% in p-$BaSi_2$/n-Si hetero-junction solar cells [6]. Thus far, a lot of studies have been carried out on $BaSi_2$ epitaxial films grown by molecular beam epitaxy (MBE). MBE is, however, not a practical method to fabricate large-area solar cells. We therefore have formed $BaSi_2$ films by sputtering. However, the electron concentration was more than 10^{19} cm^{-3}, and therefore the photoresponsivity was very small for $BaSi_2$ films, which were formed by radio-frequency (RF) magnetron sputtering at room temperature (RT) and post annealing at 600 °C [7]. In this work, we formed $BaSi_2$ films directly on a heated Si(111) substrate by sputtering. We first investigated the dependence of Ba to Si atomic ratio of a deposited film on pressure (P). We achieved the formation of 150-nm-thick poly-crystalline $BaSi_2$ films directly on a Si (111) substrate heated at 600 °C using helicon-wave excited plasma (HWP) sputtering. The photoresponsivity was drastically enhanced by approximately 400 times compared to those reported [7].

2. Experiment

Si(111) substrates were loaded into the HWP sputtering system (ULVAC, MB00-1014) after cleaning the substrates. The polycrystalline $BaSi_2$ target, made by Tosoh Corporation, was used. In the first experiment, the P was varied from 0.25–3.0 Pa, and the flow rate of Ar was set at 10 sccm. The RF power was set at 100 W. The samples were covered with 20-nm-thick Al to prevent oxidation. The atomic ratio was measured by Rutherford backscattering (RBS) measurements. As described later, the obtained Ba atomic ratio was deficient from stoichiometry, and hence two or three small pieces of platelike Ba (1.0×1.0 cm^2) was added on the $BaSi_2$ target.

In the second experiment, we attempted to form $BaSi_2$ films at a heated Si(111) substrate at 600 °C. Crystalline quality of the grown layers was characterized using Raman spectroscopy. For photoresponsivity measurement, a 3-nm-thick a-Si capping layer was formed to prevent oxidation [3]. 80-nm-thick indium tin oxide (ITO) surface electrodes with a diameter of 1 mm and Al rear electrodes were fabricated by RF sputtering. The heavily doped n$^+$-Si(111) substrate ($\rho < 0.01$ Ωcm) was used to make the contribution of photogenerated carrier in the Si substrate negligible. The carrier concentration was measured using high-resistivity n-Si (111) (ρ=1000-10000Ωcm) substrate to prevent Si substrate signal at RT by the van der Pauw method.

3. Result and discussion

Figure 1(a) shows the RBS atomic ratio of Ba and Si atoms of the films sputtered at RT. The dotted lines and the solid lines present results sputtered without and with the 1.0 cm^2 platelike Ba source on the $BaSi_2$ target, respectively. The Si atomic ratio of the film sputtered at $P = 0.25$ Pa was more than 85%, and gradually decreased with increasing P. However, the Si atomic ratio was more than 66.7% even at $P = 3.0$ Pa, that is more than the Si atomic ratio of the $BaSi_2$ target. In the formation of $BaSi_2$ films on a heated Si substrate, the diffusion of Si atoms from the Si substrate occurs [8]. Hence, the Si atomic ratio deposited at RT should be smaller than 66.7% at a given P to form $BaSi_2$ directly on a heated Si substrate. As shown in the solid line in Fig. 1, the Si atomic ratio decreased by putting one Ba source on the target in the whole range of P, meaning that the addition of the Ba sources on the target is a practical means to increase the Ba atomic ratio of the sputtered film. As shown in Fig. 1(b), the deposition rate of the film decreased significantly with P. The Ba/Si atomic ratio and the deposition rate of the sputtered film depend significantly on P. This is caused by the difference in atomic weight among Si, Ar, and Ba atoms, which are 28.08, 39.95, and 137.33, respectively.

Figure 2 shows grazing-incidence (GI) 2θ X-ray diffraction (GI-XRD) patterns with Cu Kα radiation of samples A and B sputtered at 600 °C and at $P = 0.25$ Pa, where the number of platelike Ba source was two and three, respectively. For reference, the calculated diffraction pattern of orthorhombic $BaSi_2$ was also shown. All the observed diffraction peaks were assigned to $BaSi_2$.

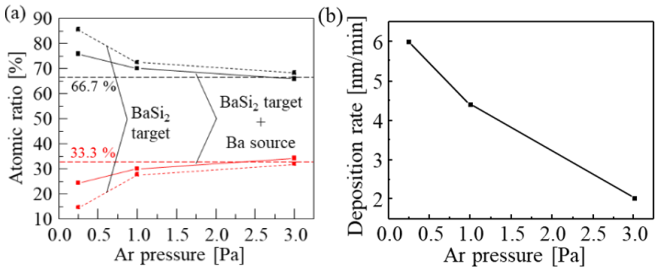

Fig. 1. (a) Ba and Si atomic ratios against P for samples sputtered without (dotted lines) and with (solid lines) the presence of Ba source on the $BaSi_2$ target, and (b) dependence of measured deposition rate of the sputtered film decreased on P by presence of the Ba source on the $BaSi_2$ target (solid lines).

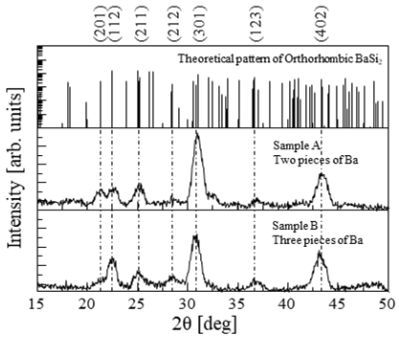

Fig. 2. GI-XRD patterns of the films sputtered at 600 °C on a Si(111) substrate by adding two or three Ba sources on the $BaSi_2$ target.

Figure 3 shows the typical example of Raman spectrum of the sample B at P = 0.25 Pa. Three pieces of Ba source were placed on the $BaSi_2$ target. The Raman lines originate from Si tetrahedra with T_h symmetry in the lattice of $BaSi_2$. Identification of Raman lines is given in Ref. [9]. The transverse optical phonon line of Si (Si_{TO}) was observed even in such a thick $BaSi_2$ film. Considering that the absorption coefficient of $BaSi_2$ at a wavelength of 532 nm is $\alpha = 3 \times 10^5$ cm^{-1} [10], and the penetration depth of the laser light is limited to around $1/\alpha \times 3 \sim 0.1$ μm, the Si_{TO} signal originated from Si precipitates in the $BaSi_2$ film. Similar Si_{TO} signals were detected in $BaSi_2$ [11,12] and β-$FeSi_2$ films [13] by Raman spectroscopy, meaning that the excess Si atoms became crystallized in the form of crystalline Si. The growth rate of $BaSi_2$ was approximately 0.4 μm per hour, which is approximately four times higher than that by MBE.

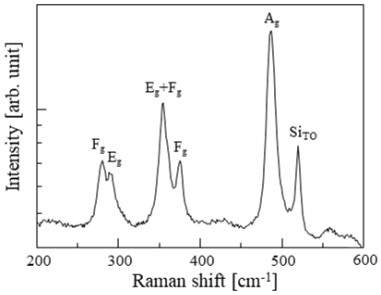

Fig. 3. Raman spectrum of sample B

Figure 4 shows the photoresponse spectra of sample B formed at P=0.25 and 0.4 Pa. Various bias voltages (V_{bias}) were applied to the front ITO electrode with respect to the Al electrode for the photogenerated holes in the n-$BaSi_2$ to be extracted to the ITO electrode. The photoresponsivity of sample B after the a-Si cap increased sharply for photons with energies greater than the band gap of $BaSi_2$ and reached 0.2A/W at 2.0 eV at V_{bias} = 0.5 V for sample formed at P=0.4 Pa. This value corresponds to EQE = 40%, and is more than 400 times higher than that previously reported [7]. Such improvement in photoresponsivity is ascribed to significant reduction of carrier concentration of the film. The electron concentration of $BaSi_2$ in sample B was 2×10^{16} cm^{-3} at RT by Hall measurement. This value is approximately two orders of magnitude smaller than that reported [7]. On the basis of these results, sputtering shows promise for use in the formation of $BaSi_2$ films.

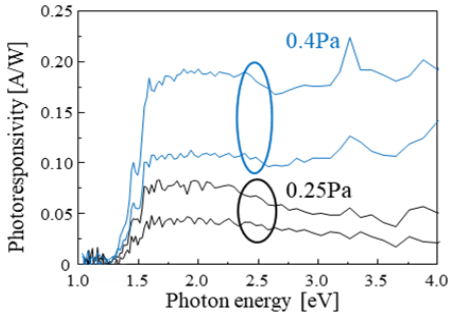

Fig. 4. Photoresponse spectra of sample B after the a-Si cap under various bias voltages.

Conclusions

Polycrystalline $BaSi_2$ films were formed by HWP using a $BaSi_2$ target. The deposited Ba to Si atomic ratio was varied in the range from approximately 1 : 9 to 1 : 2 by increasing the vacuum level from 0.25 to 3.0 Pa during the sputtering. By putting small pieces of platelike Ba sources on the $BaSi_2$ target during the sputtering, we succeeded to form approximately 150-nm-thick orthorhombic $BaSi_2$ films on a heated Si(111) substrate at 600 °C. The formation of $BaSi_2$ was evidenced by x-ray diffraction and Raman spectroscopy. The photoresponsivity was distinctly improved and reached 0.2A/W at 2.0 eV at at V_{bias} = 0.5 V.

References

[1] J. Evers *et al.*, Chem. Int. Ed. Eng. 16 (1977) 659.
[2] M. Imai *et al*, J. Alloys Compd. 224 (1995) 111.
[3] K. Morita *et al.*, Thin Solid Films 508(2006) 363.
[4] M. Baba *et al.*, J. Appl. Phys. 120 (2016) 085311.
[5] K. O. Hara *et al.*, Appl. Phys. Express 6 (2013) 112302.
[6] S. Yachi *et al.*, Appl. Phys. Lett. 109 (2016) 072103.
[7] T. Yoneyama *et al.*, Thin Solid Films 534 (2013) 116.
[8] R. Takabe *et al.*, J. Appl. Phys. 123 (2018) 045703.
[9] Y. Terai *et al.*, Jpn. J. Appl. Phys. 56 (2017) 05DD02.
[10] K. Toh *et al.*, Jpn. J. Appl. Phys. 50 (2011) 068001.
[11] R. Takabe *et al.*, J. Appl. Phys. 123 (2018) 045703.
[12] Y. Terai *et al.*, Jpn. J. Appl. Phys. 56 (2017) 05DD02.
[13] M. Iinuma *et al.*, Jpn. J. Appl. Phys. Conf. Proc. 5 (2017) 01110