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著者別名	都甲 薫, 末益 崇
journal or publication title	Applied physics letters
volume	100
number	15
page range	152114
year	2012
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URL	http://hdl.handle.net/2241/117057

doi: 10.1063/1.3703585

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Citation: *Appl. Phys. Lett.* **100**, 152114 (2012); doi: 10.1063/1.3703585

View online: <http://dx.doi.org/10.1063/1.3703585>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v100/i15>

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Improved photoresponsivity of semiconducting BaSi₂ epitaxial films grown on a tunnel junction for thin-film solar cells

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(Received 28 February 2012; accepted 26 March 2012; published online 13 April 2012)

The highest photoresponsivity and an internal quantum efficiency exceeding 70% at 1.55 eV were achieved for 400 nm thick undoped *n*-type BaSi₂ epitaxial layers formed on a *n*⁺-BaSi₂/*p*⁺-Si tunnel junction (TJ) on Si(111). The diffusion of Sb atoms was effectively suppressed by an intermediate polycrystalline Si layer grown by solid phase epitaxy, located between the TJ and undoped BaSi₂ layers. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3703585>]

Recently, thin-film solar cell materials, such as CuIn_{1-x}Ga_xSe₂ (CIGS), CdTe, and organic materials have been attracting increasing attention due to their high efficiency and low cost. In contrast, the optical absorption layers of crystalline Si (c-Si) solar cells tend to be much thicker than conventional thin-film solar cells, such as CIGS, because the optical absorption coefficient α is much smaller for crystalline Si. Therefore, Si-based materials for high-efficiency thin-film solar cells have received significant interest. However, little steadfast effort has been devoted to any materials other than Si, CIGS, and CdTe and III-V compounds as far as inorganic semiconductors are concerned. Among such materials, we have focused much attention on semiconducting BaSi₂.^{1,2} The bandgap of BaSi₂ is approximately 1.3 eV³⁻⁵ and can be increased up to 1.4 eV in Ba_{1-x}Sr_xSi₂,^{6,7} which matches the ideal solar spectrum much better than crystalline Si. In addition, BaSi₂ has a very large absorption coefficient of approximately $3 \times 10^4 \text{ cm}^{-1}$ at 1.5 eV.⁵ A large value of α and expansion of the bandgap in Ba_{1-x}Sr_xSi₂ were theoretically expected.⁸⁻¹⁰ BaSi₂ can be grown epitaxially on Si(111) substrates by molecular beam epitaxy (MBE) due to the small lattice mismatch of approximately 1% between the BaSi₂ and Si(111) planes.¹¹⁻¹⁴ Recently, we have achieved large photoresponsivities for photon energies greater than the bandgap from BaSi₂ epitaxial layers on Si(111) and polycrystalline BaSi₂ layers on $\langle 111 \rangle$ -oriented Si films deposited on SiO₂ using an Al-induced crystallization method.^{15,16} However, due to large conduction and valence band discontinuities at the BaSi₂/Si heterointerface,¹⁷ a tunnel junction (TJ) is necessary to assist current flow in a BaSi₂ *pn* junction diode formed on a Si substrate. In our previous work, we formed a Sb-doped *n*⁺-BaSi₂/*p*⁺-Si TJ and achieved clear photoresponsivities in undoped *n*-BaSi₂ overlayers formed on the TJ.¹⁸⁻²⁰ Thus, the only remaining process was the formation of *p*-type BaSi₂ on the *n*-BaSi₂ layer to complete the BaSi₂ *pn* junction diode. However, the photoresponsivities obtained were much smaller than expected, less than 0.1 A/W. Detailed examination of the Sb concentration in the undoped BaSi₂ layers on the TJ revealed that a significant amount of Sb atoms diffused into the undoped BaSi₂ overlayers.²¹ This may lead to a shorter lifetime and thus a smaller diffusion length of minority carriers, which would result in deterioration of the TJ properties and reduction in the photoresponsivity. Sb atoms are

known to diffuse into the Si overlayers of Si/Sb/Si structures formed by MBE.²² Nakagawa *et al.* overcame this problem by employing solid phase epitaxy (SPE);²³ amorphous SiGe layers were deposited onto the Sb-adsorbed SiGe layer with subsequent annealing to transform the amorphous layers into the crystalline phase. However, there has been no report on a growth method to prevent Sb segregation in semiconducting silicides. In this letter, we report the highest photoresponsivities ever achieved for semiconducting silicides, corresponding to an internal quantum efficiency exceeding 70%, by adopting a growth method to suppress Sb atom diffusion. This was accomplished by placing a thin intermediate Si layer grown by SPE between the TJ and the undoped BaSi₂ layer.

An ion-pumped MBE system equipped with standard Knudsen cells for Ba and Sb sources and an electron-beam evaporation source for Si was used for the growth of BaSi₂ films. An approximately 25 nm thick Sb-doped *n*⁺-BaSi₂ layer was grown by MBE at 490 °C on a heavily boron doped *p*⁺/*p*-Si substrate ($N_A \sim 3 \times 10^{19} \text{ cm}^{-3}$).^{18,24} A 10 nm thick amorphous Si (a-Si) layer was then deposited onto the *n*⁺-BaSi₂ layer at room temperature (RT), followed by annealing at 650 °C for 1 min to transform the a-Si into crystalline Si by SPE. The c-Si layer was changed into BaSi₂ by Ba deposition at 520 °C. Finally, an approximately 400 nm thick undoped BaSi₂ layer was grown by MBE at 490 °C (sample A). Details of the SPE growth procedure are provided in a previous report.²¹ For comparison, another sample (sample B) was prepared without the SPE layer. For measurements of the current-voltage (*I*-*V*) characteristics and photoresponse properties, a thin capping layer of Sb-doped *n*⁺-BaSi₂ was grown on top of the undoped BaSi₂ layers to form ohmic contacts. Stripe-shaped Au/Cr ohmic contacts were deposited by vacuum evaporation on the top surface, and Al ohmic contacts were sputtered on the backside. No anti-reflection (AR) coating was deposited. The photocurrent was evaluated at RT using a lock-in technique that employed a xenon lamp with a 25 cm focal-length single monochromator (Bunko Keiki, SM-1700 A). The reflectance spectrum was evaluated with a reflection/transmission measurement system using a xenon lamp with an integrating sphere. The light grazed the sample at an incident angle of 5°.

Figure 1(a) shows the *I*-*V* characteristics of the samples measured at RT. Bias voltages were applied to the *p*⁺-Si

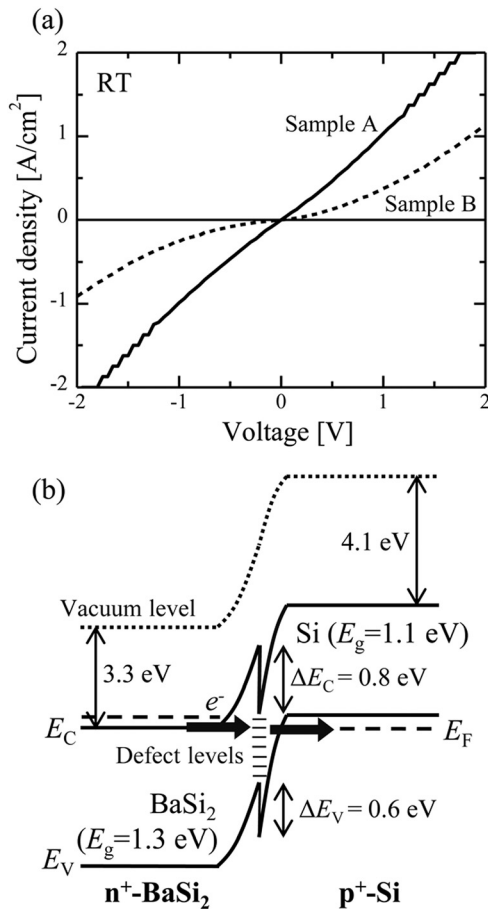


FIG. 1. (a) I - V characteristics of samples A and B measured at RT. The bias voltage was applied to the p^+ -Si substrate with respect to the top surface. (b) Schematic of the forward-biased n^+ -BaSi₂/ p^+ -Si TJ and the tunneling process.

substrate with respect to the top n^+ -BaSi₂ surface. The linear I - V characteristics of sample A indicate that the sample behaves like a constant resistance under the bias voltage. This means that most of the bias voltage was applied to the undoped BaSi₂ region but not to the TJ due to its excellent tunneling properties. Even under a very small bias voltage, the carriers could still easily tunnel through the n^+ -BaSi₂/ p^+ -Si hetero-junction without being blocked. In contrast, the series resistance under a small bias was more than 2 times larger in sample B, which suggests that part of the bias voltage was applied to the TJ to assist tunneling. Secondary ion mass spectroscopy (SIMS) measurements using Cs ions were performed to compare the Sb concentration in samples A and B. Reference samples with a controlled number of Sb atoms doped in BaSi₂ have not yet been prepared but will be necessary to precisely determine the impurity concentration by SIMS. Although exact Sb concentrations could not be obtained, the Sb concentration in the undoped BaSi₂ layer in sample A was determined to be smaller than that in sample B by more than one order of magnitude. Therefore, we conclude that the diffusion of Sb atoms not only decreases the resistance of the undoped layer but also deteriorates the quality of the TJ in sample B. In addition, the I - V characteristics of both samples exhibited good symmetry and no negative differential resistance effect was observed under forward bias conditions, as is often the case with heavily doped

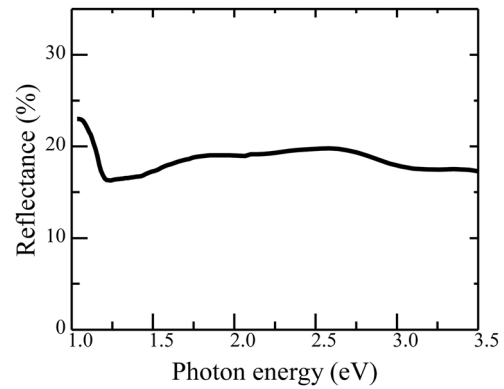


FIG. 2. Reflectance spectrum of BaSi₂ epilayers grown on a Si(111) substrate.

n^+ / p^+ junctions. Thus, we speculate that there are many defect levels at the n^+ -BaSi₂/ p^+ -Si heterointerface, as shown in Fig. 1(b), due to the different crystal structures and lattice constants of BaSi₂ and Si, and thereby, tunneling is likely to occur via the localized states in the forbidden gap rather than by direct tunneling from band to band.

Figure 2 shows a typical reflectance spectrum for BaSi₂ epitaxial layers grown on a Si(111) substrate. BaSi₂ has a reflectance, R , smaller than 20% for photon energies in the range from 1.2 to 3.5 eV. The smaller R enables more photons to enter the BaSi₂ layer, thereby enlarging the photocurrent. The relatively constant value of R over the entire visible range makes it a simple task to determine an appropriate thickness for the AR coating layer deposited on the surface of BaSi₂.

Figure 3(a) shows the photoresponse spectra for samples A and B (inset) measured at RT under various bias voltages. The dashed lines indicate the external quantum efficiencies (EQE). For sample A, light absorption produces electron-hole pairs that are separated by the electric field and drift to the electrodes, which leads to a current flow in the external circuit. Photocurrents were observed for photon energies greater than 1.25 eV and increased sharply for photon energies greater than 1.3 eV, reaching a maximum photoresponsivity of 0.37 A/W at 1.55 eV when the bias voltage was 2.0 V. These values are the highest ever reported for semiconducting silicides and are more than three times higher than the value of 0.1 A/W at 0.98 eV obtained for a bulk n -type β -FeSi₂ single crystal.²⁵ Compared with the result for sample B, the photoresponsivity is increased by more than 30 times. This is attributed to suppression of the thermal diffusion of Sb atoms in the BaSi₂ layers due to the presence of the c -Si layer grown by SPE, and the resulting heavier Sb concentration in the n^+ -BaSi₂ layer enables the formation of the high-quality TJ in sample A. The diffusion length of minority carriers would be much longer in sample A than in sample B, due to the lower Sb concentration in the undoped BaSi₂ layer. The contribution of photoexcited carriers in the p^+ -Si substrate to the measured photocurrent can be neglected, because of the amount of absorption in Si is small compared with BaSi₂, and also the photoexcited electrons (minority carriers in p^+ -Si) easily recombine with holes before reaching the electrodes. It should be noted that in the photoresponse spectra, other peaks become pronounced at

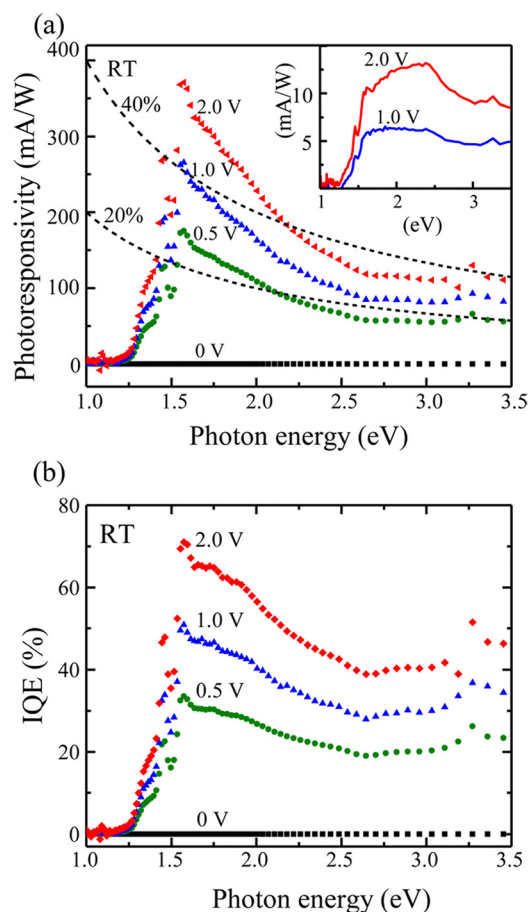


FIG. 3. (a) Photoresponse spectra of samples A and B (inset) measured at RT for various bias voltages. The dashed lines indicate the EQE. (b) IQE as a function of photon energy measured for sample A.

photon energies of 1.46 and 3.25 eV. This is due to the non-linear property of the photocurrent caused by the intense line-shaped spectrum of the xenon light at these photon energies. The EQE increased to 40% under a bias voltage of 1.0 V and increased further to 60% under a bias voltage of 2.0 V at 1.55 eV. Figure 3(b) shows the internal quantum efficiency (IQE) as a function of the photon energy for sample A, determined from EQE divided by $1 - R$. The IQE reached a maximum of over 70% under a bias voltage of 2.0 V at 1.55 eV. This value could be further improved to beyond 90% by increasing the thickness of the absorption layer (undoped BaSi₂ layer) from 400 nm to 3 μ m, assuming $\alpha = 3 \times 10^4 \text{ cm}^{-1}$ at 1.55 eV.

In summary, 400 nm thick undoped *n*-type BaSi₂ epitaxial layers were fabricated on a *n*⁺-BaSi₂/*p*⁺-Si TJ formed on Si(111) by MBE. The photoresponse reached a maximum at 1.55 eV. The photoresponsivity (IQE) was increased from 0.17 A/W (33%) to 0.37 A/W (71%) at 1.55 eV when the

bias voltage was increased from 0.5 to 2.0 V. These values are the highest ever reported for semiconducting silicides, due to the effective suppression of Sb atom diffusion by the intermediate *c*-Si layer grown using the SPE technique.

This work was financially supported in part by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency (JST).

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