# Investigation of native defects in $BaSi_2$ epitaxial films by electron paramagnetic resonance

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We investigated photoresponse, photoluminescence (PL), and electron paramagnetic resonance (EPR) spectra of 0.5 μm-thick $BaSi_2$ films grown by molecular beam epitaxy using various Ba-to-Si deposition rate ratios ($R_{Ba}/R_{Si}$). $BaSi_2$ films ($R_{Ba}/R_{Si}$ = 2.2) showed the highest photoresponsivity at room temperature. In contrast, $BaSi_2$ films with $R_{Ba}/R_{Si}$ away from 2.2 showed low photoresponsivity but intense sub-bandgap PL at 9 K. An anisotropic EPR line was observed below 20 K for such $BaSi_2$ films. The EPR line disappeared for $BaSi_2$ films passivated with atomic hydrogen. Thereby, the PL and EPR signals are interpreted to originate from native defects in the $BaSi_2$ films.

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Various materials have been studied as candidates for solar cell applications to solve increasing future energy demand.[1-4] Among them, we have paid special attention to barium disilicide ($BaSi_2$) consisting of earth-abundant elements.[5,6] In $BaSi_2$, following the Zintl-Klemm concept, one Ba atom supplies two valence electrons to one Si atom. As a result, four Si atoms connect with each other by covalent bonding and form a tetrahedron, $(Si_4)^{4-}$, in its crystal structure.[7] This environmentally friendly material possesses an indirect bandgap of 1.3 eV,[8,9] matching the solar spectrum better than crystalline Si (c-Si) for a single-junction solar cell. In addition, it shows a high optical absorption coefficient $\alpha = 3 \times 10^4\ \mathrm{cm}^{-1}$ at 1.5 eV (more than 40 times as large as that of c-Si) in spite of indirect band gap.[10] Furthermore, $BaSi_2$ has a sufficiently large minority-carrier diffusion length ($L \approx 10$ μm) and a large minority-carrier lifetime ($\tau \sim 10$ μs).[11-15] Based on its bipolar doping properties,[16-19] we have achieved conversion efficiencies ($\eta$) approaching 10% in p-$BaSi_2$/n-Si heterojunction solar cells[20-22] and have recently demonstrated the operation of homojunction solar cells.[23, 24] To achieve higher $\eta$ in $BaSi_2$-pn homojunction solar cells, the fabrication of high-quality $BaSi_2$ light absorbing layers is urgently required. Actually, the Ba-to-Si deposition rate ratios ($R_{Ba}/R_{Si}$) during molecular beam epitaxy (MBE) significantly affect their carrier concentrations and photoresposivities.[25] According to first-principles calculations by Kumar *et al.*,[19] Si vacancies ($V_{Si}$) are mostly likely to exist as native point defects in $BaSi_2$. Deep level transient spectroscopy and Raman spectroscopy measurements also indicated the existence of $V_{Si}$ near the $BaSi_2$/Si interfaces,[26] and in the surface regions,[27] respectively. Recently, we found that an introduction of atomic hydrogen (H) into the $BaSi_2$ films by radio-frequency plasma led to a marked improvement of photoresponsivity and minority carrier lifetime owing to hydrogen passivation of $V_{Si}$.[28] However, experimental evidence showing the existence of $V_{Si}$ or other defects in $BaSi_2$ films is quite limited.[29] Electron paramagnetic resonance (EPR) is considered one of the most powerful techniques to detect defects which carry a charge and have a spin ($S \neq 0$). One of its main advantages is its very good sensitivity since it is possible to study samples containing only $10^{-13}$ mol of paramagnetic centers.[30] Each center is characterized by a $g$ tensor which determines the intensity of its Zeeman energy under static magnetic field. In c-Si, for instance, many defects have been found and their local structures have been determined by EPR.[31-39] In this article, we aim to unambiguously detect paramagnetic defects in $BaSi_2$ epitaxial films by continuous wave EPR. Furthermore, we examine the effect of atomic H on the defect properties of $BaSi_2$ films by combining EPR with photoluminescence (PL) spectroscopy.

We used an MBE system equipped with an electron-beam evaporation source for 10N-Si and standard Knudsen cells for 3N-Ba. Floating zone (FZ) n-Si(111) substrate (resistivity $\rho$ > 10000 Ωcm) were used for EPR measurement. On the other hand, Czochralski (CZ) n-Si(111) substrates ($\rho$ < 0.01 Ωcm) were used for photoresponsivity measurement to make a contribution of photogenerated carriers in the Si substrate negligible. We grew 0.5 μm-thick $BaSi_2$ epitaxial layers by MBE at 580 °C. Details of the growth procedure of $BaSi_2$ films were reported previously.[25] During the MBE growth, $R_{Si}$ was fixed to be 0.9 nm/min and $R_{Ba}$ was varied from 0.9 to 3.6 nm/min, giving a variation of $R_{Ba}/R_{Si}$ from 1.0 to 4.0. Epitaxial growth of $a$-axis-oriented $BaSi_2$ was confirmed from the $\theta$–$2\theta$ x-ray diffraction (XRD; Rigaku Smart Lab) and reflection high-energy electron diffraction patterns. For another sample, we supplied atomic H produced by a radio-frequency plasma gun for 15 min to a 0.5 μm-thick $BaSi_2$ epitaxial layer ($R_{Ba}/R_{Si}$ = 2.2) at 580 °C.[28] Photoresponse spectra were evaluated at room temperature (RT) using a lock-in technique with a xenon lamp and a 25-cm-focal-length single monochromator (Bunko Keiki SM-1700A and RU-60N). We applied a bias voltage $V_{bias}$ to the front indium-tin-oxide (ITO) electrode with respect to the backside Al electrode. PL measurements were carried out at 9 K with the excitation laser light of 442 nm and detected by a liquid nitrogen cooled InP/InGaAs photomultiplier (Hamamatsu Photonics R5509-72) and amplified by the lock-in technique. For the EPR experiments, the samples have been cut to a typical size of 1.0

× 0.2 × 0.06 $cm^3$ and were transferred into an EPR tube. These tubes were sealed under Ar atmosphere. X-band (~9.65 GHz) EPR spectra were recorded at 10–20 K with a Bruker EMX spectrometer equipped with an ESR 900 helium flow cryostat (Oxford instruments) controlled by an ITC503 (Oxford Instrument) and an ER-4116 dual mode cavity. Due to the use of a field modulation and lock-in detection, spectra were obtained as the derivative of absorption. Sample preparation details are shown in Table I.

Table I. Sample preparation details. Si substrate, $BaSi_2$ layer thicknesses, $R_{Ba}/R_{Si}$, and atomic hydrogen supply duration $t_H$ are given.

| Sample | Si substrate | $BaSi_2$ layer | $R_{Ba}/R_{Si}$ | $t_H$ |
|---|---|---|---|---|
| A | CZ $n^+$-Si(111), $\rho < 0.01$ Ωcm | 0.5 μm | 1.0 | – |
| B | CZ $n^+$-Si(111), $\rho < 0.01$ Ωcm | 0.5 μm | 2.2 | – |
| C | CZ $n^+$-Si(111), $\rho < 0.01$ Ωcm | 0.5 μm | 4.0 | – |
| D | FZ n-Si(111), $\rho > 10^4$ Ωcm | – | – | – |
| E | FZ n-Si(111), $\rho > 10^4$ Ωcm | 0.5 μm | 2.2 | – |
| F | FZ n-Si(111), $\rho > 10^4$ Ωcm | 0.5 μm | 2.2 | 15 min |
| G | CZ $n^+$-Si(111), $\rho < 0.01$ Ωcm | 0.5 μm | 2.2 | 15 min |
| H | CZ $n^+$-Si(111), $\rho < 0.01$ Ωcm | 0.3 μm | 2.2 | 15 min |

Figure 1(a) shows the photoresponse spectra of samples A-C, $BaSi_2$ films with $R_{Ba}/R_{Si}$ = 1.0, 2.2, and 4.0, respectively, at RT. Figure 1(b) presents their PL spectra at 9 K. The photoresponsivity increased sharply for photon energies higher than the band gap of $BaSi_2$ in Fig. 1(a). Sample C, $BaSi_2$ films ($R_{Ba}/R_{Si}$ = 4.0), showed the smallest photoresponsivity, whereas the PL intensity of this sample was the highest in Fig. 1(b). The penetration depth of the excitation laser light in PL is estimated to be $3/\alpha \sim 50$ nm. Therefore, most of the photons are generated in the $BaSi_2$ films by the front-side excited PL. Sub-bandgap PL with a peak energy at around 1.0 eV in Fig. 1(b) therefore indicates the transition of electrons between localized states within the band gap, caused by defects in $BaSi_2$ films.[40] We speculate that the $BaSi_2$ film ($R_{Ba}/R_{Si}$ = 4.0) in sample C contains a lot of $V_{Si}$ because it was grown under Si poor condition. The PL spectra were well reproduced by two Gaussians curves located at 0.82 (0.84) and 0.92 (1.00) eV for $R_{Ba}/R_{Si}$ = 2.2 (1.0), and three Gaussian curves at 0.86, 1.00, and 1.04 eV for $R_{Ba}/R_{Si}$ = 4.0. These results indicate that different native defects were formed in the $BaSi_2$ films grown under different values of $R_{Ba}/R_{Si}$ as discussed previously.[19,25,27] Kishino *et al*. also observed sub-bandgap PL originating from the defects in $BaSi_2$ single crystals.[41] We chose sample B out of samples A-C hereafter, because it showed the highest photoresponsivity and thus we considered sample E to be worthy of investigation by EPR. Sample E contains *a*-axis-orientated $BaSi_2$ epitaxial films using the same growth conditions as sample B, but fabricated on the FZ-Si substrate for EPR measurement.

We measured angular dependence of EPR spectra at 15 K for sample D (FZ-Si substrate) and sample E ($R_{Ba}/R_{Si}$ = 2.2). As shown in Fig. 2(a), we varied the angle $\theta$ between the $BaSi_2$ *a*-axis and the static magnetic field, $B_0$, from 0° (*a* axis is parallel to $B_0$) to 90° (*a* axis is normal to $B_0$). Although we used the high-$\rho$ FZ-Si substrate in order to minimize EPR lines originating from the Si substrate, we observed an *isotropic* EPR line at $g$ = 2.007 in Fig. 2(b). On the other hand, in sample E, in addition to the same line, we observed additional *anisotropic* EPR signals marked by triangles in Fig. 2(c).

The isotropic EPR line obtained for the FZ-Si substrate, sample D, in Fig. 2(b) can be fitted by the first derivative of one Lorentzian function as shown in Fig. 3(a). Regarding the EPR lines from the Si substrates, a large number of EPR lines have been reported. However, it is sufficient to consider only $P_b$ center,[33] E' center,[37] $P_{s0}$ and $P_{s1}$ centers,[38] and damaged Si-surface center[39] because FZ-Si(111) substrates were employed in this work. Among them, it can be concluded that the EPR line observed from the Si substrate originates from damaged Si-surface centers because of its anisotropy and its $g$ value.[39] These centers are caused by microcracks of a Si substrate on its cleavage planes. Note here that we did not observe $P_b$ centers in the Si substrates used. $P_b$ center is well known as a paramagnetic center caused by dangling bonds on Si surfaces. Present results indicate that the number of $P_b$ center was too small to be detected.

Figure 3(b) shows one of the results shown in Fig. 2(c) ($\theta = 0°$). We also measured the EPR spectrum of sample F, passivated with atomic H (Fig. 3(c)). Comparing with sample E, to our surprise, the additional EPR lines have disappeared in sample F. A depth profile of H atoms by secondary ion mass spectrometry (SIMS) showed that H atoms were uniformly distributed only in the $BaSi_2$ film (Fig. 3(d)). Also, the sub-bandgap PL decreased drastically in sample G as shown in Fig. 4, while a marked enhancement of photoresponsivity was observed for sample G, grown under the same growth conditions as sample F, but on the CZ-Si substrate.[28] Therefore, it is reasonable to consider that atomic H affects the defects inside the $BaSi_2$ films. These experiments are highly significant because they prove that the additional lines found in sample E come from defects inside the $BaSi_2$ film and that these defects are passivated by atomic H.

To obtain better characterizations of the additional EPR lines in the $BaSi_2$ film (sample E), we tentatively fit the spectra with three species, here simulated with three Lorentzian derivatives. One of these species correspond to the isotropic line from the substrate (red line) while the two others (Defects 1 and 2, orange and blue lines) correspond to defects in $BaSi_2$ films. At 20K (Fig. 5(a)) Defect 2 is easy to follow on the complete angle range and show a pronounced $g$ anisotropy (from 2.004 to 2.011). Defect 1 is more difficult to be detected and its angular variation is more difficult to analyze. It must be noted that Defects 1 and 2 anisotropy can be easily understood: even if $BaSi_2$ domains exhibit disordered *b*- and *c*-axes orientation in plane, all *a* axes are orientated perpendicular to the $BaSi_2$ epitaxial film. Thus, it is possible to detect $g$ variation in these systems with an angular dependence from a static magnetic field parallel to *a*-axis to a static magnetic field perpendicular to *a*-axis, as described in this article. This anisotropy is thus in complete agreement with a defect's origin in the $BaSi_2$ epitaxial film.

In conclusion, we fabricated 0.5 μm-thick $BaSi_2$ films with $R_{Ba}/R_{Si} = 2.2$ by MBE and performed EPR and PL measurements. We observed the two anisotropic EPR lines in $BaSi_2$ films. These lines disappeared after the introduction of atomic hydrogen. Additionally, their $g$ values were distinguished from other paramagnetic centers reported in Si. Hence, we concluded that these EPR lines are ascribed to defects inside the $BaSi_2$ film. This is a direct evidence that the improvement on photoresponsivity have been realized by decreasing the concentration of the defects in the film.

To the best of our knowledge, it is the first detection of paramagnetic defects in $BaSi_2$ by EPR. Such results pave the way to further and more detailed spectroscopic studies using advanced EPR techniques (multifrequency EPR, pulsed EPR). Given the contribution of these techniques to knowledge of defects in more classical material (Si), we can expect very interesting outcomes in the near future.

## ACKNOWLEDGEMENTS

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Fig. 1 (a) Photoresponse and (b) PL spectra of samples A-C, 0.5-μm-thick $BaSi_2$ with $R_{Ba}/R_{Si}$ varied as 1.0, 2.2, and 4.0, respectively. The photoresponse spectra were measured at RT under a bias voltage of −1.0 V applied to the front ITO electrode with respect to the back Al electrode. PL spectra were measured at 9 K. Each PL spectrum is reproducible by two or three Gaussians curves as shown in the inserted in (b). Broken line shows the position of the band gap of $BaSi_2$ (1.3 eV). Reprinted with permission from (a) Takabe *et al*., J. Appl. Phys. **123**, 045703 (2018). Copyright 2019 AIP Publishing LLC.[15]

Fig. 2 (a) Schematic drawings of sample arrangement. The angle between the *a*-axis of epitaxial $BaSi_2$ films and applied static magnetic field was changed from 0° (upper) to 90° (lower) with an interval of 15°. Angle dependence of EPR spectra of (b) FZ-Si (sample D) and (c) $BaSi_2$ films (sample E). Additional EPR lines marked by triangles appeared in (c).

Fig. 3 EPR spectra measured at 15 K for (a) sample D, (b) sample E, and (c) sample F. Additional EPR lines denoted by orange solid line and blue dot line in sample E disappeared after the introduction of atomic H in sample F. (d) SIMS depth profile of H atoms and secondary ions (Ba and Si) for sample H grown under the same conditions as sample F.

Fig. 4 PL spectra of samples B and G at 9 K. Sub-bandgap PL disappeared after the introduction of atomic H in sample G. The inset shows the significant improvement of photoresponsivity in sample G.

Fig. 5 Angle dependent EPR spectra measured at 20 K on sample E at (a) $\theta$ = 0°, (b) $\theta$ = 45°, and (c) $\theta$ = 90°. Red broken line, blue dot line, and orange solid line reproduce measured spectra. (b) Variations of paramagnetic centers against $\theta$. Each origin is discussed in the text.