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# Simple way of finding Ba to Si deposition rate ratios for high photoresponsivity in BaSi<sub>2</sub> films by Raman spectroscopy

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Since the photoresponsivity of BaSi<sub>2</sub> is sensitive to a Ba-to-Si deposition rate ratio ( $R_{\text{Ba}}/R_{\text{Si}}$ ), there is a need to determine the optimum value of  $R_{\text{Ba}}/R_{\text{Si}}$ . We grew 0.5 μm-thick BaSi<sub>2</sub> films with  $R_{\text{Ba}}/R_{\text{Si}}$  varied from 1.1–3.6 at 580 °C and 0.4–4.7 and 650 °C. The photoresponsivity reached a maximum at  $R_{\text{Ba}}/R_{\text{Si}} = 2.2$  and 1.2, respectively. Raman spectroscopy revealed that the crystalline quality of BaSi<sub>2</sub> became better with decreasing  $R_{\text{Ba}}/R_{\text{Si}}$ . However, as  $R_{\text{Ba}}/R_{\text{Si}}$  decreased further beyond these values, excess Si precipitated, showing that the optimum value of  $R_{\text{Ba}}/R_{\text{Si}}$  should be as small as possible without causing Si precipitates to form.

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We have focused on semiconducting barium disilicide ( $\text{BaSi}_2$ ) as a new candidate for solar cell applications,<sup>1</sup> because it possesses attractive properties such as a suitable bandgap for solar cells ( $\sim 1.3$  eV), a high optical absorption coefficient  $\alpha = 3 \times 10^4 \text{ cm}^{-3}$  at 1.5 eV (more than 40 times as large as that of crystalline Si),<sup>2-5</sup> a large minority-carrier diffusion length  $L \approx 10 \text{ }\mu\text{m}$ ,<sup>6</sup> and bipolar doping properties.<sup>7-10</sup> We have achieved energy conversion efficiencies  $\eta$  approaching 10% in p- $\text{BaSi}_2$ /n-Si heterojunction solar cells,<sup>11-13</sup> which are among the highest performances ever reported for solar cells based on semiconducting silicides. Our next target is  $\text{BaSi}_2$ -pn homojunction solar cells, for which  $\eta$  is expected to exceed 25% according to calculations.<sup>14</sup> Recently, we have reported the operation of homojunction solar cells.<sup>15,16</sup> To achieve solar cells having a high- $\eta$  requires the formation of high-quality  $\text{BaSi}_2$  light absorbing materials with a low defect density. In our previous work,<sup>17</sup> we reported that undoped  $\text{BaSi}_2$  shows n-type conductivity, and the carrier type, carrier concentration, and photoresponsivity of  $\text{BaSi}_2$  change markedly depending on the Ba-to-Si deposition rate ratio ( $R_{\text{Ba}}/R_{\text{Si}}$ ); the photoresponsivity reaches a maximum, and the carrier concentration reaches a minimum at  $R_{\text{Ba}}/R_{\text{Si}} = 2.2$  when  $\text{BaSi}_2$  films were grown at 580 °C by molecular beam epitaxy (MBE). However, deep level transient spectroscopy (DLTS) studies have revealed that such  $\text{BaSi}_2$  films still contain defects.<sup>18</sup> First-principles calculations based on VASP code show that Si vacancies ( $V_{\text{Si}}$ ) are most likely to occur in  $\text{BaSi}_2$ ,<sup>10</sup> and that these vacancies give rise to localized states within bandgaps. DLTS measurement suggests the presence of point defects rather than extended defects.<sup>18</sup> Therefore, we consider that the defect levels detected by DLTS are caused by  $V_{\text{Si}}$  and related defects. However, there have been no reports to date in which vacancy-type defects like  $V_{\text{Si}}$  are directly detected. In this work, we first investigated the dependence of  $R_{\text{Ba}}/R_{\text{Si}}$  on the concentration and/or size of vacancy-type defects using positron annihilation spectroscopy. Positron annihilation spectroscopy is a nondestructive technique suitable for detecting vacancy-type defects in semiconductors and obtaining information on the structure of defects.<sup>19,20</sup> We

next increased the substrate temperature ( $T_S$ ) during epitaxial growth of  $\text{BaSi}_2$ . This is to compensate for defects by promoting the diffusion of Si atoms from the Si substrate into the grown layers and enhancing the migration of deposited Si and Ba atoms.

We used an MBE system equipped with an electron-beam evaporation source for 10N-Si and standard Knudsen cells for 3N-Ba. We used floating zone (FZ) n-Si(111) substrate (resistivity  $\rho > 10000 \text{ } \Omega\text{cm}$ ) for positron annihilation spectroscopy and Czochralski(Cz) n-Si(111) substrate ( $\rho < 0.01 \text{ } \Omega\text{cm}$ ) for photoresponsivity measurements to ensure that the contribution of photogenerated carriers in the Si substrate to the photoresponsivity was negligibly small. We grew 0.5  $\mu\text{m}$ -thick  $\text{BaSi}_2$  epitaxial layers by MBE at  $T_S = 580$  or  $650 \text{ } ^\circ\text{C}$ . Details of the growth procedure of  $\text{BaSi}_2$  films were reported previously.<sup>17,23</sup> During the MBE growth,  $R_{\text{Si}}$  was fixed to be 0.9 nm/min and  $R_{\text{Ba}}$  was varied from 0.9 to 3.2 nm/min, giving a variation of  $R_{\text{Ba}}/R_{\text{Si}}$  from 1.1 to 3.6. In this study, we also conducted MBE at  $650 \text{ } ^\circ\text{C}$ , which is  $70 \text{ } ^\circ\text{C}$  higher than the temperature used in our previous experiments. We expect that higher  $T_S$  promotes the diffusion of Si atoms from the Si substrate. The  $R_{\text{Ba}}/R_{\text{Si}}$  ratio was varied from 0.4 to 4.7. We then formed a 3-nm-thick a-Si capping layer in situ at  $180 \text{ } ^\circ\text{C}$ , which acted as a surface passivation layer.<sup>21</sup> Finally, indium-tin oxide (ITO) electrodes with a diameter of 1-mm and a thickness of 80 nm were sputtered onto the surface, and Al electrodes were formed on the entire back surface.

Reflection high-energy electron diffraction (RHEED) and x-ray diffraction (XRD; Rigaku Smart Lab) analyses have been used to characterize the crystalline quality of the grown layers. Epitaxial growth of  $a$ -axis oriented  $\text{BaSi}_2$  was confirmed from the  $\theta$ - $2\theta$  XRD patterns. The full width at half maximum (FWHM) of the  $\text{BaSi}_2$  600 peak was measured from the  $\omega$ -scan rocking curve to evaluate the crystal orientation of  $\text{BaSi}_2$  films. Photoresponsivity was evaluated at room temperature (RT) with the use of a lock-in technique with a xenon lamp and a 25-cm-focal-length single monochromator (Bunko Keiki SM-1700A and RU-60N). Raman

spectra were measured with a laser Raman spectrometer (JASCO, NRS-5100) based on a frequency doubled Nd:YAG laser (532 nm) at RT. Doppler broadening-positron annihilation spectroscopy was used for defect characterization, and the  $S$  parameter was evaluated. Details of this spectroscopy have been reported in ref. 22. In general, the characteristic value of  $S$  expected for the annihilation of positrons due to their trapping by vacancy-type defects is larger than that for positrons annihilated from the free-state. Through this method, vacancy-type defects of various semiconductors (i.e., GaN, AlON<sub>x</sub>, CIGS) have been investigated.<sup>22-26</sup>

Figure 1(a) shows the  $S$  parameters of BaSi<sub>2</sub> films grown at  $T_S = 580$  °C with various  $R_{Ba}/R_{Si}$ . We found that the optical properties changed markedly as  $R_{Ba}/R_{Si}$  values were varied, and the maximum photoresponsivity was achieved at  $R_{Ba}/R_{Si} = 2.2$  for samples grown at  $T_S = 580$  °C, as shown in Fig. 1(a).<sup>17</sup> Moreover, the carrier concentration reached a minimum at  $R_{Ba}/R_{Si} = 2.2$  [Fig. 1(b)].<sup>17</sup> Figure 1(b) shows the dependence of the  $S$  parameter on  $R_{Ba}/R_{Si}$ . The  $S$  parameter reached a minimum at approximately  $R_{Ba}/R_{Si} = 2.2$ , and increased when  $R_{Ba}/R_{Si}$  decreased or increased from this value. The present results suggest that vacancy-type defects which trap positrons are increased when the value of  $R_{Ba}/R_{Si}$  departs from 2.2, and they yield electrons. To decrease the vacancy-type defects in BaSi<sub>2</sub> films, we next increased  $T_S$  during MBE, and used photoresponsivity as a measure of their optical properties.

Thus far, we have set the growth temperature during MBE at  $T_S = 580$  °C, prioritizing the crystal orientation of BaSi<sub>2</sub> in the surface normal direction.<sup>27</sup> In this experiment, we increased  $T_S$  by 70 °C to 650 °C. Figure 2(a) shows the  $\theta$ - $2\theta$  XRD and RHEED patterns after MBE for BaSi<sub>2</sub> films formed with different values of  $R_{Ba}/R_{Si}$ . As shown in Fig. 2(a), sharp streaky RHEED patterns and intense  $a$ -axis-oriented diffraction peaks in the XRD patterns were observed at  $R_{Ba}/R_{Si} = 2.3$ – $4.7$ , namely, for samples under a Ba-rich condition. Conversely, as  $R_{Ba}/R_{Si}$  decreased, the intensity of  $a$ -axis-oriented diffraction peaks decreased, and the RHEED streak patterns became diffuse. A halo pattern appeared at  $R_{Ba}/R_{Si} = 0.4$  and  $0.9$ , indicating that

BaSi<sub>2</sub> was not formed. Figure 2(b) shows the  $R_{\text{Ba}}/R_{\text{Si}}$  dependence of the FWHM values obtained from the  $\omega$ -scan x-ray rocking curve using a BaSi<sub>2</sub> 600 diffraction peak. The FWHM reached a minimum at  $R_{\text{Ba}}/R_{\text{Si}} = 3.7$  (3) for the 650 (580) °C samples. Smaller FWHM means higher  $a$ -axis-orientation of BaSi<sub>2</sub> films. The optimum  $R_{\text{Ba}}/R_{\text{Si}}$  shifted to a Ba-rich side for growth at an elevated temperature, wherein diffusion of Si atoms from the Si substrate was promoted compared with growth at  $T_{\text{S}} = 580$  °C. This result indicates that the crystal orientation was determined by the Ba/Si atomic ratio. Conversely, the FWHM increased with decreasing  $R_{\text{Ba}}/R_{\text{Si}}$ , indicating that the  $a$ -axis orientation deteriorated for samples grown under Si-rich conditions. We note that the optimum  $R_{\text{Ba}}/R_{\text{Si}}$  determined from the viewpoint of crystal orientation was different from that determined from the photoresponsivity (i.e.,  $R_{\text{Ba}}/R_{\text{Si}} = 3$  and 2.2, respectively, for the 580 °C samples).

Photoresponse spectra of the samples grown at  $T_{\text{S}} = 650$  °C are shown in Fig. 3. A bias voltage  $V_{\text{bias}} = -0.5$  V was applied to the front-surface ITO electrode with respect to the back-surface Al electrode to extract the photogenerated holes in the BaSi<sub>2</sub> film to the ITO electrode. The photoresponsivity reached a maximum of approximately 1.2 A/W at 790 nm at  $R_{\text{Ba}}/R_{\text{Si}} = 1.2$ . This photoresponsivity is approximately 3 times as high as that reported previously for a sample at  $T_{\text{S}} = 580$  °C, denoted by a broken line. This improvement is interpreted to originate from the decrease of vacancy-type defects in the BaSi<sub>2</sub> films. We note that for the samples grown at 650 °C the optimum  $R_{\text{Ba}}/R_{\text{Si}}$  shifted to the Si-rich side compared with those grown at 580 °C ( $R_{\text{Ba}}/R_{\text{Si}} = 2.2$ ), as shown in Fig. 1. Hence, the density of defects unexpectedly decreased at  $R_{\text{Ba}}/R_{\text{Si}} = 1.2$ . As shown in Fig. 2(b), the optimum value of  $R_{\text{Ba}}/R_{\text{Si}}$  shifted to a Ba-rich side from the viewpoint of  $a$ -axis orientation, in comparing the 580 and 650 °C samples. To find how to determine the optimum  $R_{\text{Ba}}/R_{\text{Si}}$  for photoresponsivity, we performed Raman spectroscopy measurements. Figures 4(a) and 4(b) show the Raman spectra of the 580 and 650 °C samples, respectively, in the range between 200 and 700 cm<sup>-1</sup> at RT. In all of the samples,

we observed five distinct peaks assigned to the internal vibrations of Si tetrahedra<sup>28-31</sup> with  $T_h$  symmetry in the lattice of BaSi<sub>2</sub>.<sup>32</sup> Here, focusing on the Si-rich side, the transverse optical phonon line of Si (Si<sub>TO</sub>) was observed at  $R_{Ba}/R_{Si} \leq 1.5$  for the 580 °C samples, wherein the photoresponsivity reached a maximum at  $R_{Ba}/R_{Si} = 2.2$ , i.e., slightly higher than 1.5. The absorption coefficient of BaSi<sub>2</sub> at a wavelength of the excited laser light (532 nm) is  $\alpha = 3 \times 10^5 \text{ cm}^{-1}$ ,<sup>2</sup> hence, the penetration depth of the laser light was limited to approximately  $1/\alpha \times 3 \approx 0.1 \text{ }\mu\text{m}$ . This value is much smaller than the BaSi<sub>2</sub> layer thickness. Thus, the Si<sub>TO</sub> signal was considered to originate from Si precipitated in the BaSi<sub>2</sub> films. For the samples grown at 650 °C, the Si<sub>TO</sub> line appeared to be more pronounced at  $R_{Ba}/R_{Si} \leq 0.9$ , and the photoresponsivity was highest at  $R_{Ba}/R_{Si} = 1.2$ , as shown in Fig. 1. This value was also a little greater than 0.9. The Raman peak from  $V_{Si}$  should appear at approximately  $480 \text{ cm}^{-1}$  according to first-principle calculations.<sup>31</sup> However, this peak wavenumber of  $V_{Si}$  is close to the most intense peak of the  $A_g$  mode in BaSi<sub>2</sub>. Therefore, we examined the FWHM value of the peak intensity of the  $A_g$  mode to confirm the presence of any contribution from  $V_{Si}$ . Figure 4(c) shows the  $R_{Ba}/R_{Si}$  dependences of the peak intensity of Si<sub>TO</sub> and the FWHM values of the peak intensity of the  $A_g$  mode. Regardless of  $T_S$ , the FWHM of  $A_g$  mode decreased with decreasing  $R_{Ba}/R_{Si}$ , when grown under Si-rich conditions, meaning that the crystalline quality of BaSi<sub>2</sub> films became improved as the  $R_{Ba}/R_{Si}$  decreased. Conversely, the peak intensity of Si<sub>TO</sub> increased sharply when the  $R_{Ba}/R_{Si}$  decreased from  $R_{Ba}/R_{Si} = 2.2$  and 1.2 at  $T_S = 580$  and 650 °C, respectively, at the Si-rich side because of an excess of Si atoms. These  $R_{Ba}/R_{Si}$  values are the same as those for highest photoresponsivity. On the basis of these experimental results, the  $R_{Ba}/R_{Si}$  ratio should be as small as possible, regardless of  $T_S$ , while avoiding formation of Si precipitates. We interpret these results as follows. By growing the BaSi<sub>2</sub> films under Si-rich conditions and thereby using small values of  $R_{Ba}/R_{Si}$ , vacancy-type defects including  $V_{Si}$  might decrease, resulting in a higher photoresponsivity. However, further reductions of  $R_{Ba}/R_{Si}$  cause precipitation of crystalline Si

particles in the grown films, giving rise to defects, which thus degrade the photoresponsivity. Raman spectroscopy is an effective means of determining the optimum  $R_{\text{Ba}}/R_{\text{Si}}$  from the viewpoint of optimizing photoresponsivity.

In summary, we fabricated 0.5  $\mu\text{m}$ -thick  $\text{BaSi}_2$  films at 580  $^\circ\text{C}$  by MBE, and investigated the dependence of  $R_{\text{Ba}}/R_{\text{Si}}$  on the  $S$  parameter with the use of positron annihilation spectroscopy. The  $S$  parameter showed the same tendency against  $R_{\text{Ba}}/R_{\text{Si}}$  as that of the electron concentration. Thus, we confirmed that vacancy-type defects yield electrons in  $\text{BaSi}_2$ . To reduce such defects, we increased  $T_{\text{S}}$  during MBE growth from 580 to 650  $^\circ\text{C}$ . The FWHM of the  $\text{BaSi}_2$  600 XRD peak reached a minimum at  $R_{\text{Ba}}/R_{\text{Si}} = 4$ , and increased sharply for samples growth under Si-rich conditions. Conversely, the photoresponsivity reached a maximum of 1.2 A/W at 790 nm when  $V_{\text{bias}} = -0.5$  V for a sample grown with  $R_{\text{Ba}}/R_{\text{Si}} = 1.2$ . This value is approximately 3 times as high as that previously reported for samples grown at 580  $^\circ\text{C}$ . The FWHM of the  $A_{\text{g}}$  mode peak, reflecting the density of  $V_{\text{Si}}$ , decreased for samples grown under Si-rich conditions, whereas the intensity of the  $\text{Si}_{\text{TO}}$  peak increased sharply at  $R_{\text{Ba}}/R_{\text{Si}} \leq 1.5$  and 0.9 for samples grown at 580 and 650  $^\circ\text{C}$ , respectively. The photoresponsivity was the highest when  $R_{\text{Ba}}/R_{\text{Si}}$  was a little larger than the point at which the  $\text{Si}_{\text{TO}}$  peak increased. We therefore conclude that we should choose  $R_{\text{Ba}}/R_{\text{Si}}$  to be as small as possible to the extent that the precipitation of c-Si is avoided.

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Fig. 1 (a) Photoresponse spectra of 0.5- $\mu\text{m}$ -thick  $\text{BaSi}_2$  grown at  $T_S = 580$  °C with various  $R_{\text{Ba}}/R_{\text{Si}}$  measured under a bias voltage of  $-1.0$  V applied to the front ITO electrode with respect to the back Al electrode.<sup>17</sup> (b) Dependences of the  $S$  parameter and carrier concentration on  $\text{BaSi}_2$  films grown at  $T_S = 580$  °C.

Fig. 2 (a)  $\theta$ - $2\theta$  XRD and RHEED patterns of  $\text{BaSi}_2$  films at  $T_S = 650$  °C with various  $R_{\text{Ba}}/R_{\text{Si}}$  values. The asterisk (\*) indicates the peak for the Si substrate used. (b)  $R_{\text{Ba}}/R_{\text{Si}}$  dependences of the FWHM of  $\text{BaSi}_2$  600 peak intensity for samples grown at  $T_S = 580$  or  $650$  °C.

Fig. 3 Photoresponse spectra of 0.5- $\mu\text{m}$ -thick  $\text{BaSi}_2$  grown at  $T_S = 650$  °C with various  $R_{\text{Ba}}/R_{\text{Si}}$  values measured under a bias voltage of  $-0.5$  V applied to the front ITO electrode with respect to the back Al electrode. Broken line shows the photoresponse spectrum for the  $580$  °C with  $R_{\text{Ba}}/R_{\text{Si}} = 2.2$ .

Fig. 4 Raman spectra of samples grown at (a)  $580$  and (b)  $650$  °C with various values of  $R_{\text{Ba}}/R_{\text{Si}}$ . Arrows show the tiny peaks due to  $\text{Si}_{\text{ITO}}$ . (c)  $R_{\text{Ba}}/R_{\text{Si}}$  dependences of the FWHM of Ag mode peak intensity at  $490\text{ cm}^{-1}$  and the  $\text{Si}_{\text{ITO}}$  peak intensity at  $520\text{ cm}^{-1}$ .

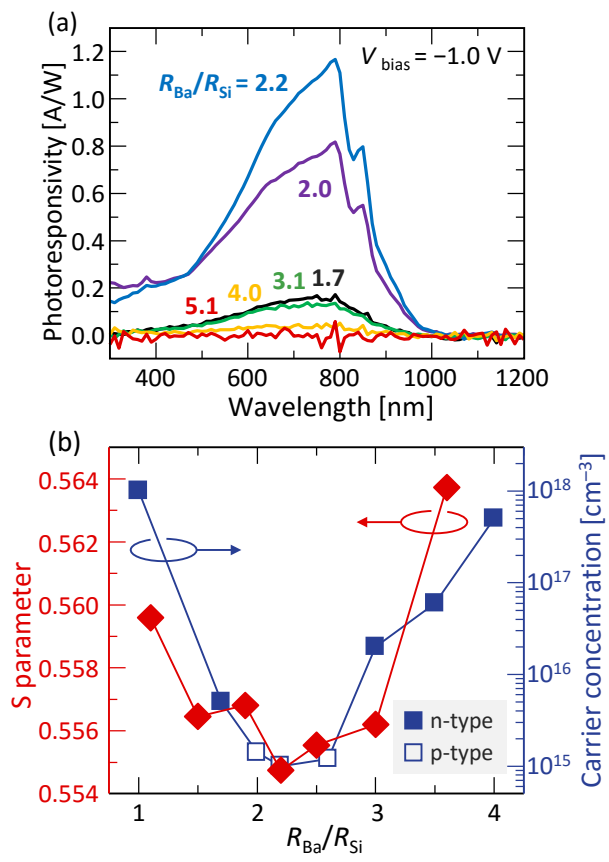


Fig. 1

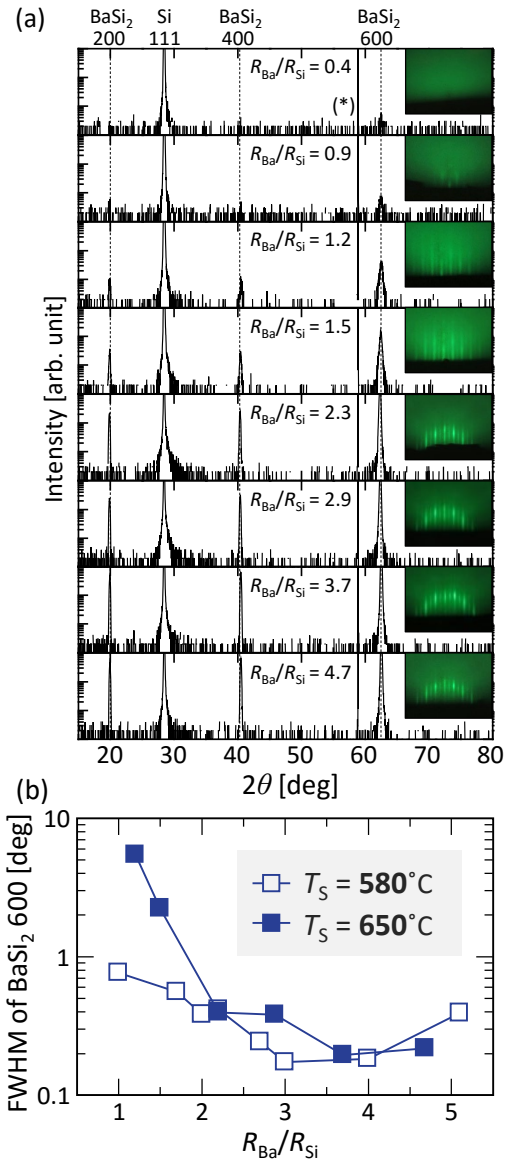


Fig. 2

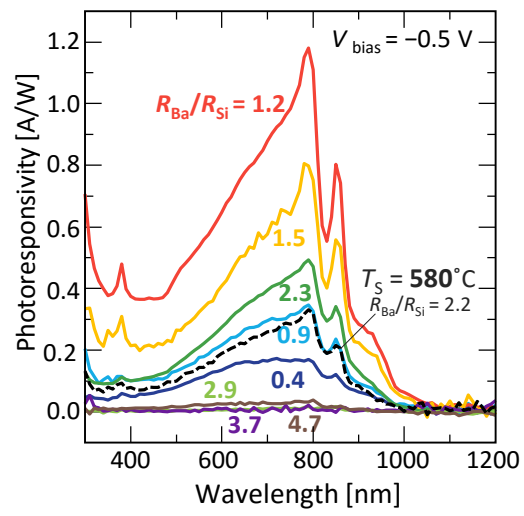


Fig. 3

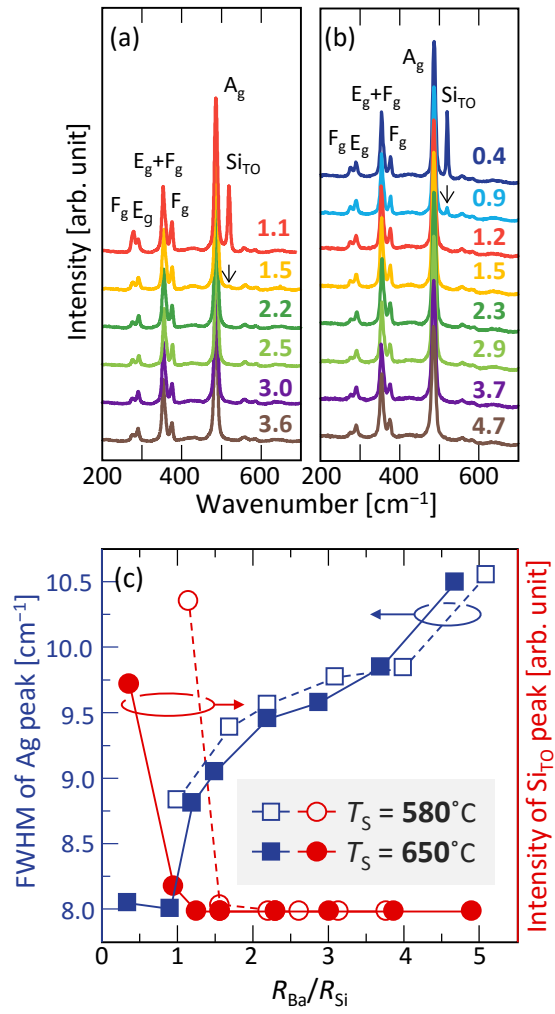


Fig. 4