Molecular beam epitaxy of boron doped p-type BaSi2 epitaxial films on Si(111) substrates for thin-film solar cells

著者別名	都甲 薫, 末益 崇
journal or publication title	Journal of crystal growth
volume	378
page range	201-204
year	2013-09
権利	(C) 2013 Elsevier B.V. NOTICE: this is the author's version of a work that was accepted for publication in Journal of crystal growth. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Journal of crystal growth, 378, 2013 http://dx.doi.org/10.1016/j.jcrysgro.2012.12.153
URL	http://hdl.handle.net/2241/119793

doi: 10.1016/j.jcrysgro.2012.12.153

Molecular beam epitaxy of boron doped *p*-type $BaSi_2$ epitaxial films on Si(111) substrates for thin-film solar cells

M. Ajmal Khan,[a] Kosuke O. Hara,[b] Kotaro Nakamura,[a] Weijie Du,[a] Masakazu Baba,[a] Katsuaki Toh,[a] Mitsushi Suzuno,[a] Kaoru Toko,[a] Noritaka Usami,[b,c] and Takashi Suemasu[a,c]

[a]*Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan*

[b]*Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan*

[c]*Japan Science and Technology Agency, CREST, Chiyoda, Tokyo 102-0075, Japan*

Corresponding author: Prof. T. Suemasu

Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

TEL/FAX: +81-29-853-5111, Email: suemasu@bk.tsukuba.ac.jp

Abstract

We have successfully grown *a*-axis-oriented *p*-type $BaSi_2$ films on Si(111) by *in situ* boron (B) doping using molecular beam epitaxy (MBE). The hole concentration in B-doped $BaSi_2$ was controlled in the range between 10^{17} and 10^{19} cm^{-3} at room temperature by changing the temperature of the B Knudsen cell crucible. The acceptor level was estimated to be approximately 23 meV.

PACS: 78.40.Fy

Keywords: B1. semiconducting silicides; B2. $BaSi_2$; B3. solar cell; A3. MBE; A1.impurity doping

1. Introduction

It is important for solar cell materials to have a large absorption coefficient and a suitable band gap to yield high conversion efficiency. Materials that are composed of abundant and non-toxic elements are also desirable. Among such materials we have focused on semiconducting $BaSi_2$. The $BaSi_2$ has the orthorhombic lattice (space group Pnma) with a unit cell containing 8 Ba and 16 Si atoms, the latter of which form Si_4 tetrahedra and can thus be considered as Zintl phase [1,2]. Semiconducting $BaSi_2$ has the indirect band gap of approximately 1.3 eV matching the solar spectrum and has a very large absorption coefficient of 3×10^4 cm^{-1} at 1.5 eV [3-5]. Optical absorption measurements have shown that the band gap of $BaSi_2$ can be increased up to 1.4 eV by replacing half of the Ba atoms in $BaSi_2$ with isoelectric Sr atoms [6], which is in agreement with the theoretical calculations [7-9]. Recently, we successfully achieved large photoresponsivity and internal quantum efficiency exceeding 70% in *a*-axis-oriented $BaSi_2$ epitaxial layers grown by molecular beam epitaxy (MBE) [10-13]. These results have spurred interest in this material. The basic structure of a solar cell is a *p*-*n* junction. Therefore, control of the conductivity of $BaSi_2$ by impurity doping is a requirement. The carrier concentration of undoped *n*-$BaSi_2$ is approximately 5×10^{15} cm^{-3} [4]. According to Imai and Watanabe [14,15], substitution of Si in the $BaSi_2$ lattice is more favorable than substitution of Ba from an energetic point of view by first-principles calculation. In our previous works, the electron concentration of Sb-doped $BaSi_2$ was

controlled in the range between 10^{16} and 10^{20} cm^{-3} at room temperature (RT). In contrast, Al- and In-doped $BaSi_2$ show *p*-type conductivity, but the hole concentration was limited up to 3×10^{17} cm^{-3} [16-19]. Thus, it is highly required to find another impurity atom for heavily *p*-type doping of $BaSi_2$. In this article, we chose to adopt boron (B) as an alternative impurity and aimed to achieve *p*-type doping of over 10^{19} cm^{-3} in $BaSi_2$ films by MBE.

2. Experimental

Details of the growth procedure for *in situ* impurity doped $BaSi_2$ films have been previously described for In- and Sb-doped $BaSi_2$ [17]. An ion-pumped MBE system equipped with standard Knudsen cells (K-cells) for Ba and B, and an electron-beam evaporation source for Si was used. For electrical measurements, high-resistivity floating-zone (FZ) *n*-Si(111) ($\rho >$ 1000 Ω·cm) substrates were used. Briefly, MBE growth of B-doped $BaSi_2$ films was carried out as follows. Firstly, a 10-nm-thick $BaSi_2$ epitaxial film was grown on Si(111) at 600 °C by reactive deposition epitaxy (RDE; Ba deposition on a hot Si substrate), and this was used as a template for the $BaSi_2$ overlayers. Next, Ba, Si, and B were co-evaporated at 600 °C onto the $BaSi_2$ template to form impurity-doped $BaSi_2$ by MBE. The thickness of the grown layers including the template was approximately 200-250 nm. The temperature of B, T_B, was varied from 1250 to 1575 °C in samples A-G. The deposition rates of Si and Ba were approximately 1.5 and 4.0 nm/min, respectively. Sample preparation was summarized in Table 1. It turned

68 out that it was difficult to make ohmic contacts with Au/Cr on as-grown B-doped $BaSi_2$ films
69 for samples grown at $T_B \leq 1500$°C. Thus rapid thermal annealing (RTA) was performed at
70 800 °C for 30 s in an Ar atmosphere with heating rate of 40°C/s for (samples C-G) prior to the
71 deposition of Au/Cr electrodes.

72 The crystal quality of the already grown layers was characterized by X-ray diffraction
73 (XRD) and reflection high-energy electron diffraction (RHEED) measurements. The electrical
74 properties were characterized by Hall measurements using the van der Pauw method. The
75 applied magnetic field was 0.5–0.7 T, normal to the sample surface. Secondary ion mass
76 spectroscopy (SIMS) measurements using O ions were performed to investigate the depth
77 profile of B doped. Reference samples with a controlled number of B atoms doped in $BaSi_2$
78 have not yet been prepared but will be necessary to precisely determine the impurity
79 concentration by SIMS.

80

81 **3. Results and discussion**

82 Figure 1 shows the θ-2θ XRD patterns of B-doped as-grown $BaSi_2$ films with
83 T_B=1250-1575 °C. The diffraction peaks of (100)-oriented $BaSi_2$, such as (200), (400) and
84 (600), are dominant in the θ-2θ XRD patterns. These peaks match the epitaxial relationship
85 between $BaSi_2$ and Si. The forbidden diffraction peak designated by (*) is considered to be
86 due to double diffraction. Further increase of T_B resulted in two new diffraction peaks of

rhombohedral B(110) around 2θ=36° and B(220) at 2θ=77°. This means that the crystalline quality starts to deteriorate with increasing the amount of B atoms in the $BaSi_2$ films. Figures 2(a)-2(h) present the streaky RHEED patterns of B-doped as-grown $BaSi_2$ films prepared with T_B=1250-1575 °C, respectively, observed along the Si[11-2] azimuth, indicating that the $BaSi_2$ films were grown successfully. Figs. 3(a) and 3(b) show the SIMS depth profiles of B concentration N_B in the B-doped as-grown $BaSi_2$ films prepared with T_B=1450 and 1550 °C, respectively. The doped B atoms are uniformly distributed in the grown layers in both samples, and they did not show any diffusion tendency. Similar results were also obtained in other samples. The averaged value of N_B for $BaSi_2$ prepared with T_B=1450 °C is approximately 2×10^{21} cm^{-3} in Fig. 3(a), while that with T_B=1550 °C is 1×10^{22} cm^{-3} in Fig. 3(b). This result is explained relatively well by the difference in vapor pressure of B; The vapor pressure of B at 1550 °C is approximately 7 times larger than that at 1450 °C [20]. These results mean that the concentration of B atoms in the $BaSi_2$ can be controlled by T_B. The B concentrations in the SIMS profiles shown in Fig. 3 were corrected using reference samples, where controlled number of B atoms was doped in the $BaSi_2$ films by ion implantations. The activation rate of B atoms can be thus estimated, that is approximately $p=10^{19}$ $cm^{-3}/N_B=10^{22}$ $cm^{-3} \cong 0.1\%$ for sample H. But it was found from plan-view transmission electron microscopy images and also from the θ-2θ XRD patterns that some amounts of B atoms were in the form of B clusters. Thus the actual B activation rate in the $BaSi_2$ film is supposed to be much higher than the

above value of 0.1%, and it is approximately 1% for sample H. The reason of such a small activation rate of B is probably attributed to relatively low growth temperature of 600°C and too much B concentrations.

We next move on to the electrical properties of B-doped as-grown $BaSi_2$ films, samples H and I. The hole concentration p was 1.0×10^{19} for sample H, and $2.5\times10^{18}cm^{-3}$ for sample I at RT. These values are the highest ever reported for p-type $BaSi_2$. We speculate that defects induced by crystallized B in the $BaSi_2$ film could cause the reduced p in sample I. In order to evaluate the acceptor level E_A in sample H, we performed the temperature dependence of p. To secure the ohmic contacts on the surface at lower temperatures, first the temperature dependence of current-voltage (I-V) characteristics were measured as shown in Fig. 4(a). Ohmic behavior was confirmed over the wide temperature range between 30 and 300 K. Resistance increases with decreasing temperature in Fig. 4(a), which is typical for semiconductors. Fig. 4(b) gives the temperature dependence of p for sample H. The acceptor level calculated using Eq. (1) was about 23 meV.

$$p \propto \exp(-\frac{E_A}{2k_BT}) \qquad (1)$$

Here, k_B is the Boltzmann's constant, and T the absolute temperature. This E_A value is much smaller than that in Al-doped $BaSi_2$ (E_A=50, and 140 meV) [18]. Such a shallow E_A level of 23 meV could be the reason for heavily p-type doing in sample H. Regarding the other samples, it was difficult to obtain reliable hole concentration and mobility data at RT. Thus,

we performed the RTA treatment on samples C-I to achieve activation of doped B atoms. The obtained p and hole mobility μ_h were summarized in Table 1. The hole concentration increases gradually from 10^{17} to 10^{19} cm^{-3} with increasing T_B, thereby showing that the RTA is a very effective means to activate the B atoms.

Figure 5 shows the measured μ_h versus p for B-doped $BaSi_2$. As the hole concentration increases the mobility decreases. This trend is usually predicted by ionized impurity scattering in conventional semiconductors. The hole mobilities are always smaller than the electron mobilities in Sb-doped $BaSi_2$ [17]. According to Migas *et al.*, this is attributed to a larger effective mass for holes than electrons [3]. The p value reached a maximum of 3.4×10^{19} cm^{-3}, and the resistivity was 0.02 Ω·cm in sample G. At present, only limited information has been obtained for the electrical properties of B-doped $BaSi_2$. We speculate that both growth temperatures during MBE and RTA duration influence the electrical properties of B-doped $BaSi_2$. Thus, further studies are necessary in order to optimize the growth condition for B-doped $BaSi_2$ films by MBE.

4. Conclusions

We achieved the hole concentration of over 10^{19} cm^{-3} at RT in *in situ* B-doped $BaSi_2$ films by MBE. The acceptor level was estimated to be approximately 23 meV from the temperature dependence of hole concentration. The RTA treatment performed at 800 °C for

30 s in Ar activated the B atoms in the $BaSi_2$ films. The hole concentration increased by the RTA treatment and reached a maximum of 3.4×10^{19} cm^{-3} for $BaSi_2$ prepared with T_B=1550 °C.

Acknowledgements

The authors would like to thanks Prof. Tanimoto of the University of Tsukuba for his kind help for XRD measurements, Dr. Imai of AIST for useful discussion. We would also like to thank Dr. Mitsushi Suzuno for the helpful discussions and valuable comments during the course of this research. This work was supported in part by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency.

References

[1] J. Evers, G. Oehlinger, A. Weiss, Angew. Chem., Int. Ed., 16 (1977) 659.

[2] M. Imai, T. Hirano, J. Alloys Compd. 224 (1995) 111.

[3] D.B. Migas, V.L. Shaposhnikov, V.E. Borisenko, Phys. Status Solidi B 244 (2007) 2611.

[4] K. Morita, Y. Inomata, T. Suemasu, Thin Solid Films 508 (2006) 363.

[5] K. Toh, T. Saito, T. Suemasu, Jpn. J. Appl. Phys. 50 (2011) 068001.

[6] K. Morita, Y. Inomata, T. Suemasu, Jpn. J. Appl. Phys. 45 (2006) L390.

[7] Y. Imai, A. Watanabe, Thin Solid Films 515 (2007) 8219.

[8] Y. Imai, A. Watanabe, Intermetallics 18 (2010) 348.

[9] Y. Imai, A. Watanabe, Intermetallics 18 (2010) 1432.

[10] W. Du, M. Suzuno, M. A Khan, K. Toh, M. Baba, K. Nakamura, K. Toko, N. Usami, T. Suemasu, Appl. Phys. Lett. 100 (2012) 152114.

[11] Y. Matsumoto, D. Tsukada, R. Sasaki, M. Takeishi, T. Suemasu, Appl. Phys. Express 2 (2009) 021101.

[12] D. Tsukada, Y. Matsumoto, R. Sasaki, M. Takeishi, T. Saito, N. Usami, T. Suemasu, Appl. Phys. Express 2 (2009) 051601.

[13] T. Saito, Y. Matsumoto, M. Suzuno, M. Takeishi, R. Sasaki, N. Usami, T. Suemasu, Appl. Phys. Express 3 (2009) 021301.

[14] Y. Imai, A. Watanabe, Intermetallics 15 (2007) 1291.

[15] Y. Imai, A. Watanabe, Intermetallics 19 (2011) 1102.

[16] M. Kobayashi, K. Morita, T. Suemasu, Thin Solid Films 515 (2007) 8242.

[17] M. Kobayashi, Y. Matsumoto, Y. Ichikawa, D. Tsukada, T. Suemasu, Appl. Physics Express 1 (2008) 051403.

[18] M. Takeishi, Y. Matsumoto, R. Sasaki, T. Saito, T. Suemasu, Physics Procedia 11 (2011) 27.

[19] M. Ajmal Khan, M. Takeishi, Y. Matsumoto, T. Saito, and T. Suemasu, Physics Procedia 11 (2011) 11.

[20] D. Stull, American Institute of Physics Handbook, Third Edition, McGraw Hill, New York, 1972.

Figure Captions

Fig. 1 θ-2θ XRD patterns of B-doped $BaSi_2$ films grown at T_B=1250-1575 °C.

Fig. 2 RHEED patterns of B-doped $BaSi_2$ films when T_B is (a) 1250, (b) 1300, (c) 1350, (d) 1400, (e) 1450, (f) 1500, (g) 1550, and (h) 1575 °C, observed along the Si[11-2] azimuth.

Fig. 3. SIMS profiles of B for $BaSi_2$ films grown at T_B= (a) 1450 and (b) 1550 °C.

Fig. 4. Temperature dependence of (a) *I-V* characteristics and (b) *p* for B-doped as-grown $BaSi_2$ films grown with T_B=1550 °C (sample G).

Fig. 5. Relationship of measured μ_h versus *p* for B-doped $BaSi_2$ films at RT.

Table 1 Sample preparation: B temperature, annealing temperature and duration during RTA, measured hole concentration and mobility are shown.

Sample	T_B (°C)	RTA	p (cm^{-3})	μ_p ($cm^2/V{\cdot}s$)
A	1250	w/o	-	-
B	1300	w/o	-	-
C	1350	800 °C /30 s	8.5×10^{16}	23
D	1400	800 °C /30 s	1.2×10^{17}	168
E	1450	800 °C /30 s	5.0×10^{17}	59
F	1500	800 °C /30 s	5.2×10^{17}	17
G	1550	800 °C /30 s	3.4×10^{19}	8.3
H	1550	w/o	1.0×10^{19}	6.3
I	1575	w/o	2.5×10^{18}	8.3

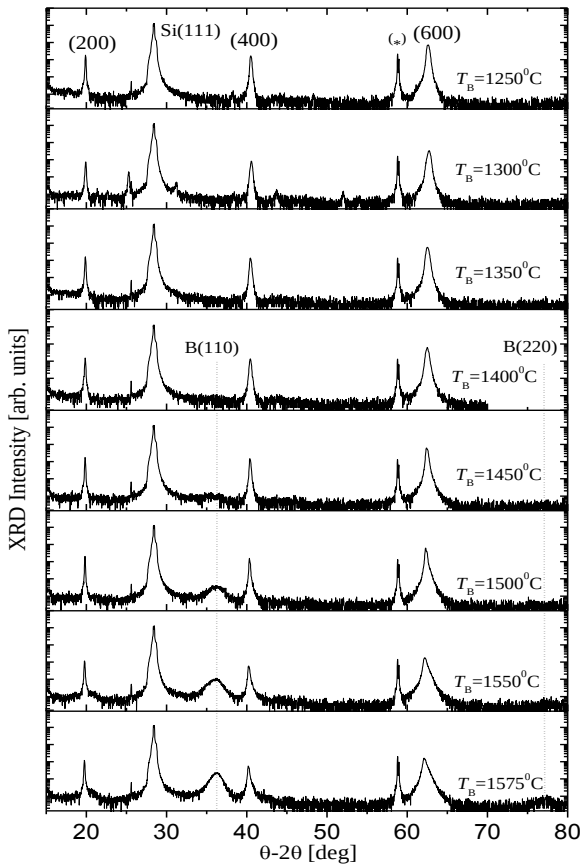
(200)
Si(111)
(400)
(*)
(600)
T_B=1250^{0}C
T_B=1300^{0}C
T_B=1350^{0}C
B(110)
B(220)
T_B=1400^{0}C
T_B=1450^{0}C
T_B=1500^{0}C
T_B=1550^{0}C
T_B=1575^{0}C
XRD Intensity [arb. units]
20
30
40
50
60
70
80
θ-2θ [deg]

Fig. 1

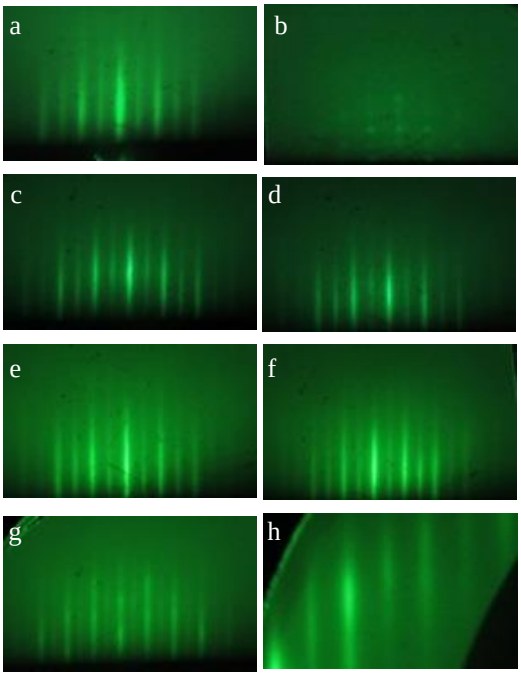

Fig. 2

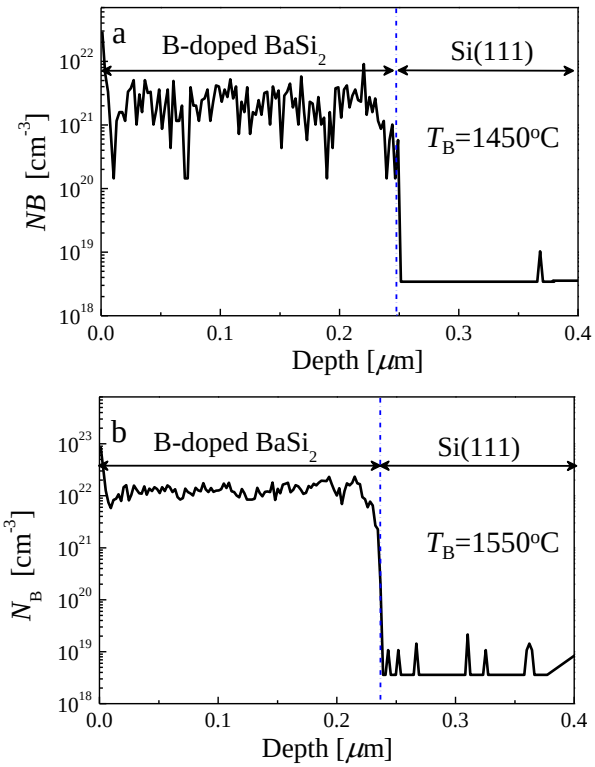
a
B-doped BaSi2
Si(111)
TB=1450oC
NB [cm-3]
Depth [μm]
b
B-doped BaSi2
Si(111)
TB=1550oC
NB [cm-3]
Depth [μm]

Fig. 3

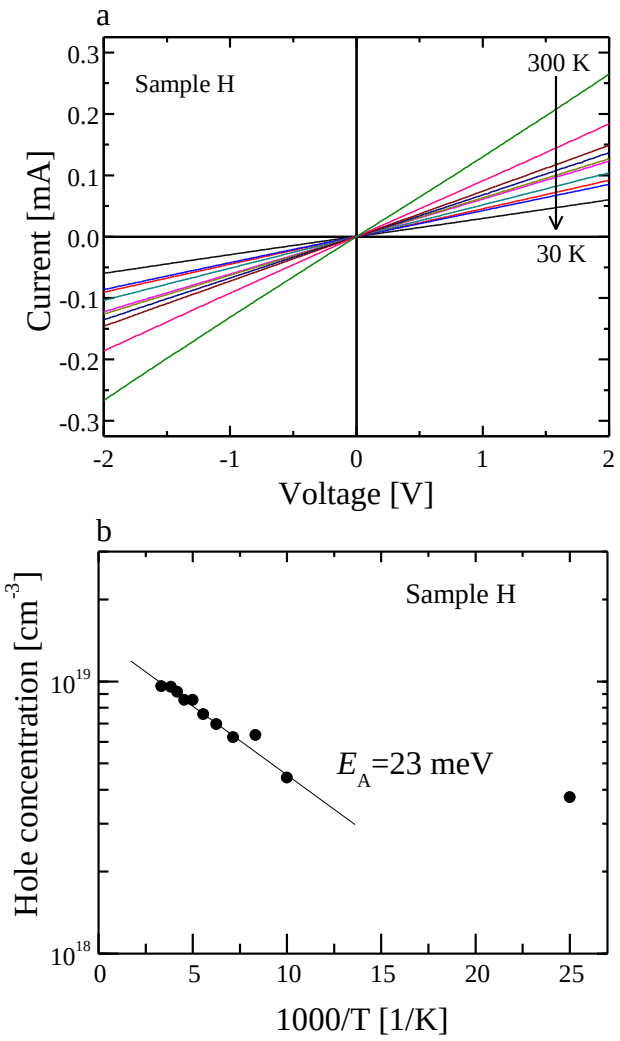
a
Sample H
300 K
30 K
Current [mA]
Voltage [V]
b
Sample H
E_A=23 meV
Hole concentration [cm^{-3}]
1000/T [1/K]

Fig. 4

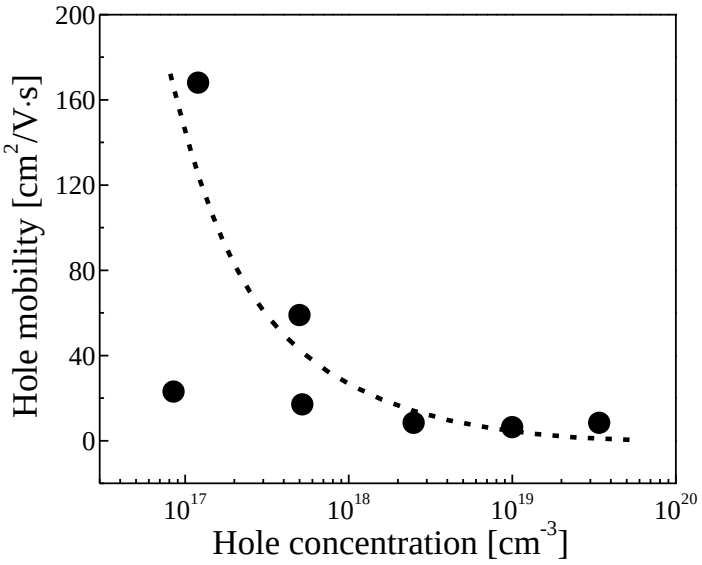
200
160
120
80
40
0
Hole mobility [cm^2/V·s]
10^{17}
10^{18}
10^{19}
10^{20}
Hole concentration [cm^{-3}]

Fig. 5