Effect of using a high-purity Fe source on the transport properties of *p*-type β-$FeSi_2$ grown by molecular-beam epitaxy

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Intentionally undoped *p*-type β-$FeSi_2$ thin films were grown on Si(111) substrates by molecular-beam epitaxy using low-purity (4N) and high-purity (5N) Fe sources to investigate the effect of using a high-purity Fe source on the electrical properties of β-$FeSi_2$. The hole mobility increased and the hole density decreased greatly as the annealing temperature and time were increased, particularly for the β-$FeSi_2$ films produced using 5N-Fe. The observed temperature dependence of the hole mobility was reproduced well by considering various carrier scattering mechanisms due to acoustic-phonon, polar-optical phonon, nonpolar-optical phonon, and ionized impurities. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2816230]

I. INTRODUCTION

β-$FeSi_2$ has been attracting considerable attention recently due to its high absorption coefficient of over 10^5 cm^{-1} at 1 eV.[1] Recent reports of light-emitting diodes operating at wavelengths used for optical-fiber communication ($\sim$1.5 μm) have served to further increase interest in β-$FeSi_2$.[2–10] β-$FeSi_2$ is also considered to be an ecologically friendly semiconductor, since both Si and Fe are nontoxic and occur abundantly in the earth's crust. β-$FeSi_2$ is therefore considered to be promising as an infrared light emitter and a detector on Si substrates. Over the past decade, a number of growth methods have been developed for fabricating β-$FeSi_2$ films.[11] However, the undoped β-$FeSi_2$ films produced by all of these methods have very large carrier densities and low mobilities, typically of the order of 10^{19} cm^{-3} and several tens of $cm^2/V\,s$, respectively, at room temperature (RT).[12] Intentionally undoped β-$FeSi_2$ films usually exhibit *p*-type conductivity except for several reports:[13,14] this is not considered to be due to impurities in low-purity (3N-4N) Fe sources behaving as dopants in β-$FeSi_2$. The hole densities in undoped β-$FeSi_2$ films are generally greater than the impurity densities in the Fe sources. Furthermore, even β-$FeSi_2$ films formed by ion-beam synthesis, which involves using mass-separated Fe^+ ions, exhibit a large hole density of approximately 10^{19} cm^{-3} at RT.[15] It seems, therefore, that there exist other origins of carriers such as Si vacancies in undoped β-$FeSi^2$ films.[16–20] In contrast to β-$FeSi_2$ films, undoped high-purity β-$FeSi_2$ single crystals show only *n*-type conductivity according to Behr *et al.*;[21] however, they also pointed out that the electrical properties of β-$FeSi_2$ single crystals were significantly influenced by deviation from the stoichiometric composition, as reported in the β-$FeSi_2$ films.[16,18–20] Thus, further studies are necessary for an improved knowledge about the nature of the intrinsic electrical properties of β-$FeSi_2$. The formation of β-$FeSi_2$ films and single crystals having low carrier densities and high mobilities at RT is critical for device applications.

There have been several reports on the transport properties of single-crystal β-$FeSi_2$.[22–24] Arushanov *et al.* explained the temperature dependence of hole mobility of β-$FeSi_2$ grown by chemical vapor transport by using acoustic, nonpolar-optical, and polar-optical phonon scatterings.[23,24] On the other hand, there is a very limited number of reports that have investigated the transport properties of β-$FeSi_2$ films in detail.[25] Very recently, Ji *et al.* described the formation of β-$FeSi_2$ films on Si(111) by molecular-beam epitaxy (MBE) using a high-purity 5N-Fe source:[26] however, the electrical properties of these films were not discussed. We have also used 5N-Fe instead of 4N-Fe and have realized a higher hole mobility and a lower hole density in undoped *p*-type β-$FeSi_2$ films grown by MBE.

The purpose of the present study is to investigate the effect of using a high-purity Fe source on the carrier density and mobility in β-$FeSi_2$ and to elucidate carrier scattering mechanisms in β-$FeSi_2$.

II. EXPERIMENTAL METHODS

An ion-pumped MBE system equipped with electron-gun evaporation sources for 10N-Si and 4N-Fe or 5N-Fe was used in this study. Production of semiconductor grade 5N-Fe was reported in detail in Refs. 27 and 28. *N*-type floating-zone Si(111) substrates with resistivities higher than 3000 Ω cm were used. After cleaning the Si(111) substrate at 850 °C for 30 min in ultrahigh vacuum, and confirming well-developed 7×7 reflection high-energy electron diffraction, an approximately 20-nm-thick highly [110]/[101]-oriented β-$FeSi_2$ epitaxial template was formed at 650 °C by reactive deposition epitaxy (RDE), that is Fe deposition on a hot Si substrate. Fe and Si were then coevaporated on the

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TABLE I. Sample preparation: purity of Fe. Growth thicknesses of RDE and MBE-grown β-$FeSi_2$ layers. Annealing conditions are also specified.

Sample	Fe	RDE/MBE (nm)	Annealing
A	4N-Fe	17/60	No
B	4N-Fe	17/60	900 °C/3 h
C	4N-Fe	17/60	900 °C/14 h
D	5N-Fe	20/180	No
E	5N-Fe	20/180	800 °C/14 h
F	5N-Fe	20/180	900 °C/14 h

template at 750 °C to form β-$FeSi_2$ continuous films by MBE.[29] Impurities such as O and Ni were significantly reduced in the 5N-Fe.

After the deposition, an approximately 100-nm-thick indium tin oxide (ITO) capping layer was deposited using a sputtering method to cover the β-$FeSi_2$ layers. The wafers were then annealed in a N_2 atmosphere at 900 °C for up to 14 h in order to improve the crystalline quality of β-$FeSi_2$.[30] The ITO capping layer prevented aggregation of the β-$FeSi_2$ film into islands. Samples were prepared as summarized in Table I. Ohmic contacts were formed on the β-$FeSi_2$ film after removing the ITO capping layer using HCl solution. The hole density and mobility were measured at temperatures between 40 and 300 K using the Van der Pauw method. The applied magnetic field was 0.7 T normal to the sample surface.

III. RESULTS AND DISCUSSION

The θ-2θ x-ray diffraction pattern of sample D is shown in Fig. 1. Highly [110] and/or [101]-oriented β-$FeSi_2$, matching the epitaxial relationship of β-$FeSi_2$ on Si(111), was formed in this sample.[31] Highly [110]/[101] orientation of β-$FeSi_2$ was also obtained in the other samples. The temperature dependence of the hole density and the hole mobility of these differently annealed samples are shown in Figs. 2 and 3. All samples showed *p*-type conduction regardless of their Fe purity. When the annealing temperature was increased from 800 to 900 °C and the annealing time became

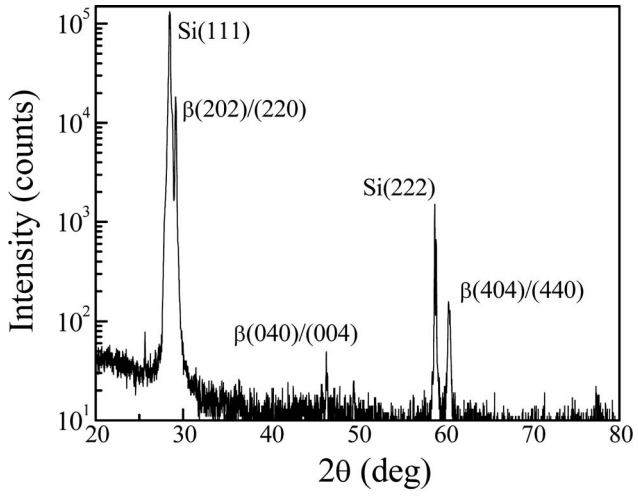

FIG. 1. θ-2θ x-ray diffraction pattern for sample D.

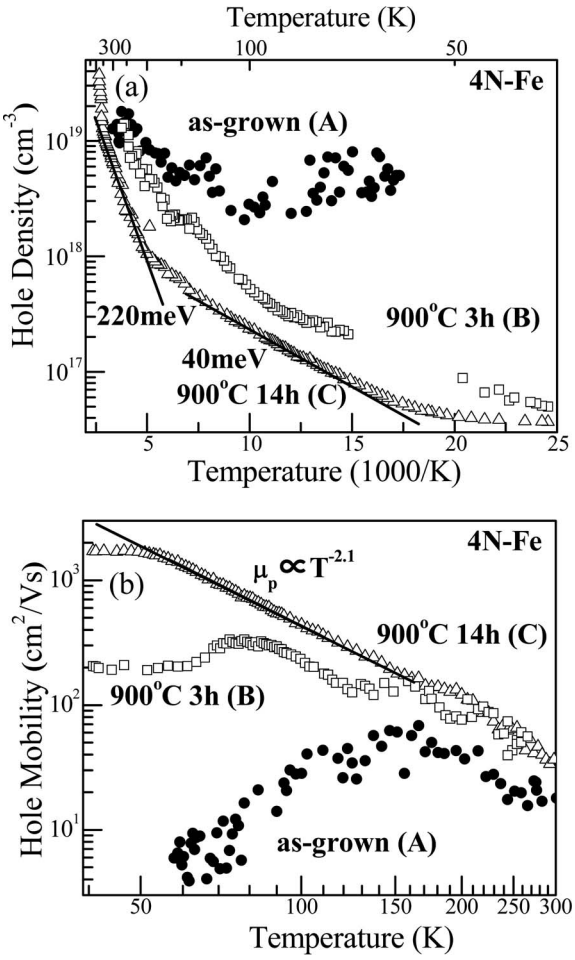

FIG. 2. Temperature dependence of (a) hole density and (b) hole mobility of the β-$FeSi_2$ films formed with 4N-Fe prepared using different annealing conditions.

longer, the hole density decreased and the hole mobility increased. It has been reported that the conduction type in undoped β-$FeSi_2$ depends on the deposited Si/Fe ratio.[16,18–20] Tani and Kido have predicted theoretically that the conduction type in undoped β-$FeSi_2$ depends on the existence of Fe and Si vacancies.[17] Electron-paramagnetic-resonance measurements of undoped *n*- and *p*-type β-$FeSi_2$ showed that Fe and Si vacancies in β-$FeSi_2$ act as donors and acceptors, respectively.[32,33] We therefore conjecture that the number of Si vacancies decreases with increasing annealing temperature and time. It should also be noted that the hole density decreased by approximately one order of magnitude from approximately 10^{19} cm^{-3} in sample C to 10^{18} cm^{-3} in sample F at RT. The hole mobility at RT was higher in sample F than in sample C. We thus speculate that impurities in the Fe source could affect the formation of Si vacancies. The mobility continued to increase with decreasing temperature; this was especially noticeable for sample F. A maximum mobility of 2300 $cm^2/V\,s$ was obtained at 40 K as shown in Fig. 3(b). On the basis of these results, we conclude that using a high-purity Fe source is an effective way to improve the electrical properties of β-$FeSi_2$. The hole mobility at RT is higher in sample A than in sample D, probably due to imhomogeneity in sample D. There is room for argument on this point.

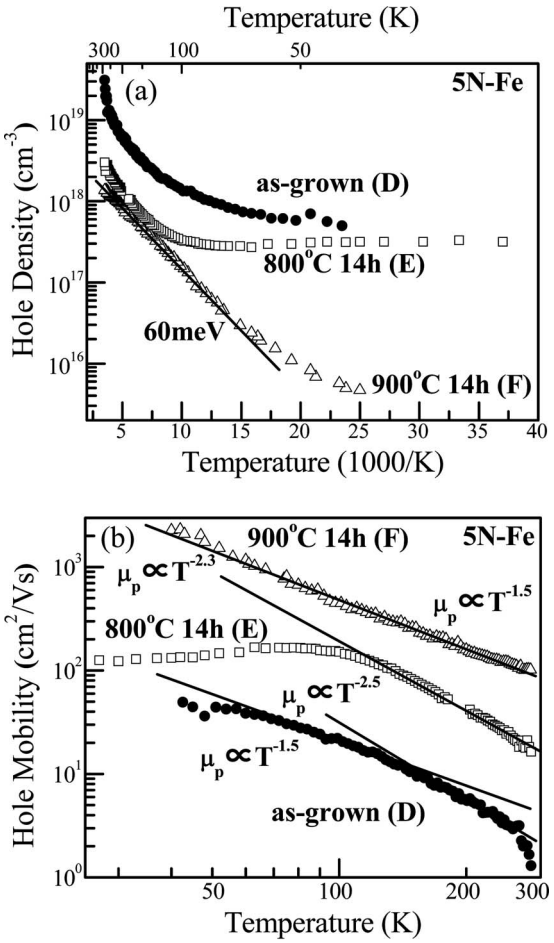

FIG. 3. Temperature dependence of (a) hole density and (b) hole mobility of the β-$FeSi_2$ films formed with 5N-Fe prepared using different annealing conditions.

Next, we discuss what kinds of carrier scattering mechanisms operate in β-$FeSi_2$. The n values (obtained by assuming that the mobility varies as $1/T^n$ at high temperatures) increased from $n=1.5$ in Fig. 2(b) to $n=2.5$ in Fig. 3(b). This demonstrates that mobility cannot be explained only by acoustic-phonon scattering ($n=1.5$). Therefore, other scattering mechanisms, such as nonpolar-optical-phonon, polar-optical-phonon, and ionized impurity scatterings, need to be considered in order to explain the high measured mobilities [see Figs. 2(b) and 3(b)].

The mobility from acoustic-phonon scattering μ_{ac} is given by[34]

$$\mu_{ac} = \frac{2\sqrt{2\pi}}{3}\frac{e\hbar^4\rho\mu_l^2}{m^{*2.5}k_B^{1.5}E_{ac}^2}T^{-1.5}, \tag{1}$$

where ρ is the density of β-$FeSi_2$ (4.93 g/cm^3), μ_l is the sound velocity in β-$FeSi_2$, m^* is the effective mass of hole, E_{ac} is the deformation potential of acoustic-phonon, T is the absolute temperature, k_B is Boltzmann's constant, and $\hbar$ is the reduced Planck's constant. The sound velocity μ_l is given by[34]

$$\mu_l \cong \frac{2\pi k_B\theta}{h}\left(\frac{V/48}{6\pi^2}\right)^{1/3}, \tag{2}$$

where θ is the Debye temperature and V is the volume of the unit cell. m^* of β-$FeSi_2$ has been reported to be between $0.6m_0$ and $1.0m_0$ and thus $m^*=0.75m_0$ was used in the analysis, where m_0 is the free electron mass. θ is taken to be 640 K.[23] As mentioned earlier, the mobilities increase with decreasing temperature as $1/T^n$ with $n>1.5$, that is, they are much stronger than for acoustic phonon scattering. Thus, we have to assume that the mobility is limited not only by acoustic phonon scattering but also by other scattering mechanisms.[24] The combined effect of the acoustic and nonpolar optical phonon scattering μ_{acnpo} is given by

$$\mu_{acnpo} = \mu_{ac}S(\theta,\eta,T), \tag{3}$$

where η is $(E_{npo}/E_{ac})^2$ and E_{npo} is the deformation potential of nonpolar-optical phonon. $S(\theta,\eta,T)$ can be approximated by

$$S(\theta,\eta,T) \approx (1+A\eta)^{-1}, \tag{4}$$

with $A=Hz/(e^z-D)$, where $z=\theta/T$ and H and D are the values determined by η. These values are described in detail in Ref. 35.

The mobility from polar-optical-phonon scattering μ_{po} is given by[34]

$$\mu_{po} = 25.4\frac{T^{0.5}}{\theta(m^*/m_0)^{1.5}}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)^{-1}(e^{\theta/T}-1) \times\left(0.4+\frac{0.148\theta}{T}\right), \tag{5}$$

where ε_0 and ε_∞ are the direct current and the high-frequency dielectric constants, respectively.

The mobility from ionized impurity scattering μ_i is given by[34]

$$\mu_i = \frac{AT^{1.5}}{N_I[\ln(1+\beta^2)-\beta^2/(1+\beta^2)]}, \tag{6}$$

where A is a constant and N_I is the density of ionized impurities. Ionized impurity scattering originates from charged particles. We think that the origin of holes in the grown films is Si vacancies in β-$FeSi_2$ as mentioned earlier. They could work as charged particles according to Ref. 17. Thus, the measured hole densities were used as N_I in the calculation. The parameter β was calculated using one of the following two equations by Brooks–Herring and Conwell–Weisskopf; which one is used depends on the value of N_I,

$$\beta_{BH} = \frac{2m^*}{\hbar}\left(\frac{2}{m^*}3k_BT\right)^{0.5}L_D \tag{7}$$

or

$$\beta_{CW} = \frac{1}{Z}\frac{\varepsilon_0}{16}\frac{T}{100}\left(\frac{2.35\times10^{19}}{N_I}\right)^{1/3}, \tag{8}$$

where L_D is the Debye length. β_{CW} and β_{BH} were used for samples C–E and sample F, respectively. These elastic mobility scatterings are described in detail in Ref. 34. The total

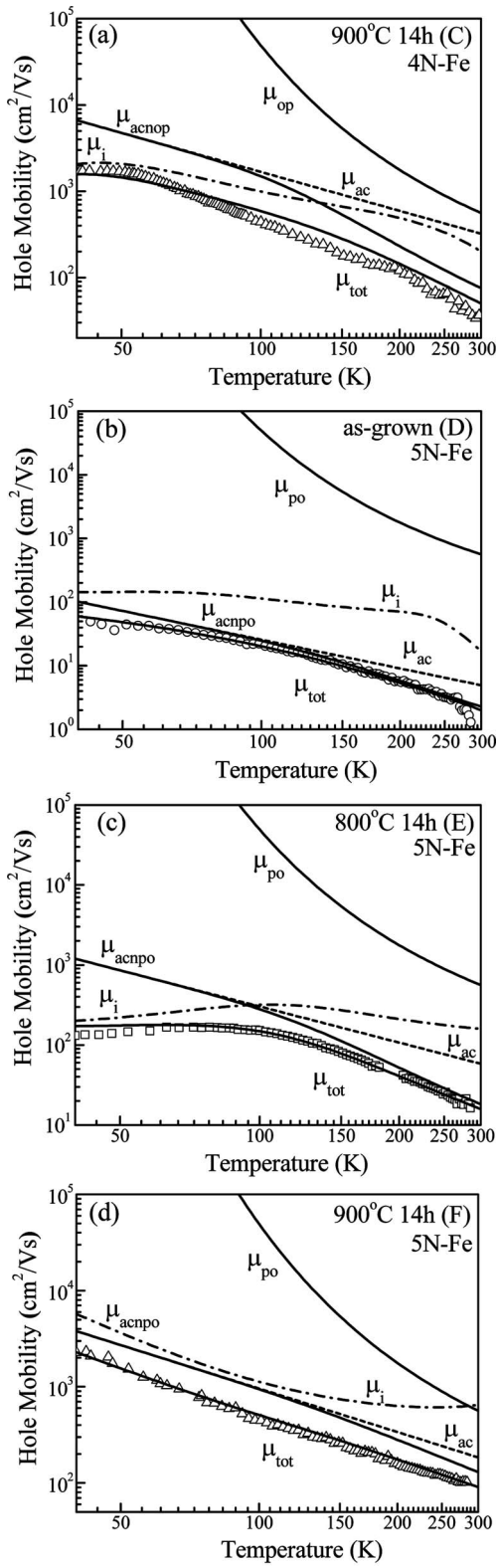

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FIG. 4. Temperature dependence of calculated and measured hole mobilities of β-$FeSi_2$ obtained for (a) sample C, (b) sample D, (c) sample E, and (d) sample F. The data points indicate experimental values. μ_{ac}, μ_{po}, μ_{acnpo}, and μ_i show the calculated mobilities from acoustic-phonon scattering, polar-optical-phonon scattering, combined effect of the acoustic and nonpolar-optical-phonon scattering, and impurity ion scattering, respectively. μ_{tot} is the total mobility.

mobility, as a function of temperature, is then given by Matthiessen's rule as

$$\beta_{tot}^{-1} = \mu_{acnpo}^{-1} + \mu_{po}^{-1} + \mu_i^{-1}. \quad (9)$$

TABLE II. Parameters used in the fit.

Sample	E_{ac} (eV)	θ (K)	m^*/m_0	ε_0	ε_∞
C	7.0	640	0.75	29.9	23
D	55	640	0.75	29.9	23
E	16	640	0.75	29.9	23
F	9.0	640	0.75	29.9	23

Figures 4(a)–4(d) show the hole mobilities calculated using Eq. (9) and the measured ones for the four samples C, D, E, and F, respectively. These figures show that the measured mobilities can be reproduced using the earlier scatterings. The parameters used in the fit are summarized in Table II. The values of ε_0=29.9 and ε_∞=23 were used for all the samples, as reported in Ref. 25. The value of E_{ac} was used as an adjustable parameter to fit the experimental results.

The earlier analysis shows that the ionized impurity or acoustic-phonon scatterings become dominant at low temperatures and the optical-phonon scattering becomes dominant at high temperatures. The higher hole mobility in the β-$FeSi_2$ formed with 5N-Fe was attributed to a reduction in the ionized impurity scattering. The value of E_{ac}, the deformation potential of acoustic phonons, decreased with increasing annealing temperature and time as shown in Table II. The decrease in E_{ac} with increasing annealing temperature and time is considered to reflect the improvement in the crystallinity of β-$FeSi_2$. In the fitting, we used the value of E_{ac} as an adjustable parameter and succeeded fitting to the experimental results. However, we think that some additional scattering mechanisms should be added in the future instead of using E_{ac} as an adjustable parameter in order to explain the effect of crystalline improvement by annealing.

IV. SUMMARY

The temperature dependence of the hole density and the hole mobility of intentionally undoped *p*-type β-$FeSi_2$ thin films grown on Si(111) substrates by MBE using low-purity (4N) and high-purity (5N) Fe sources was investigated. The hole mobility decreased down to approximately 10^{18} cm^{-3} and the hole mobility exceeded 100 $cm^2/V\,s$ at RT after annealing at 900 °C for 14 h for β-$FeSi_2$ formed with 5N-Fe. These values were approximately one order of magnitude smaller and three times higher than those obtained for β-$FeSi_2$ formed with 4N-Fe, respectively. Good fits to the measured temperature dependences of the hole mobility were obtained by considering various scattering mechanisms. From the analysis, it was found that ionized impurity scattering was significantly lower in β-$FeSi_2$ formed with 5N-Fe compared with that formed with 4N-Fe.

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[1]M. C. Bost and J. E. Mahan, J. Appl. Phys. **64**, 2034 (1988).
[2]D. Leong, M. Harry, K. J. Reeson, and K. P. Homewood, Nature (London) **387**, 686 (1997).
[3]T. Suemasu, Y. Negishi, K. Takakura, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **39**, L1013 (2000).
[4]M. A. Lourenco, T. M. Butler, A. K. Kewell, R. M. Gwilliam, K. J. Kirkby, and K. P. Homewood, Jpn. J. Appl. Phys., Part 1 **40**, 4041 (2001).
[5]L. Martinelli, E. Grilli, M. Guzzi, and M. G. Grimaldi, Appl. Phys. Lett. **83**, 794 (2003).
[6]S. Chu, T. Hirohada, H. Kan, and T. Hiruma, Jpn. J. Appl. Phys., Part 2 **43**, L154 (2004).
[7]M. Takauji, C. Li, T. Suemasu, and F. Hasegawa, Jpn. J. Appl. Phys., Part 1 **44**, 2483 (2005).
[8]T. Sunohara, C. Li, Y. Ozawa, T. Suemasu, and F. Hasegawa, Jpn. J. Appl. Phys., Part 1 **44**, 3951 (2005).
[9]C. Li, T. Suemasu, and F. Hasegawa, J. Appl. Phys. **97**, 043529 (2005).
[10]S. Murase, T. Sunohara, and T. Suemasu, J. Cryst. Growth **301–302**, 676 (2007).
[11]V. E. Borisenko, *Semiconducting Silicide* (Springer, New York, 2000).
[12]D. J. Oostra, C. W. T. Bulle-Lieuwma, D. E. W. Vandenhoudt, F. Felten, and J. C. Jans, J. Appl. Phys. **74**, 4347 (1993).
[13]Z. Liu, M. Osamura, T. Ootsuka, S. Wang, R. Kuroda, Y. Fukuzawa, Y. Suzuki, T. Mise, N. Otogawa, Y. Nakayama, H. Tanoue, and Y. Makita, Jpn. J. Appl. Phys., Part 2 **43**, L504 (2004).
[14]Z. Liu, M. Osamura, T. Ootsuka, R. Kuroda, Y. Fukuzawa, T. Mise, N. Otogawa, Y. Nakayama, H. Tanoue, and Y. Makita, Jpn. J. Appl. Phys., Part 2 **44**, L261 (2005).
[15]Y. Maeda, K. Miyake, and K. Ohashi, Rev. Laser Eng. **28**, 93 (2000) (in Japanese).
[16]M. Komabayashi, K. Hijikata, and S. Ido, Jpn. J. Appl. Phys., Part 1 **29**, 1118 (1990).
[17]J. Tani and H. Kido, J. Alloys Compd. **352**, 153 (2003).
[18]K. Takakura, T. Suemasu, Y. Ikura, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **39**, L789 (2000).
[19]K. Takakura, T. Suemasu, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **40**, L249 (2001).
[20]T. Suemasu, K. Takakura, C. Li, Y. Ozawa, Y. Kumagai, and F. Hasegawa, Thin Solid Films **461**, 209 (2004).
[21]T. G. Behr, J. Werner, G. Weise, A. Heinrich, A. Burkokv, and C. Gladun, Phys. Status Solidi A **160**, 549 (1997).
[22]Ch. Kloc, E. Arushanov, M. Wendl, H. Hohl, U. Malang, and E. Bucher, J. Alloys Compd. **219**, 93 (1995).
[23]E. Arushanov, H. Lange, and J. Werner, Phys. Status Solidi A **166**, 853 (1998).
[24]E. Arushanov, L. Ivanenko, H. Vinzelberg, D. Eckert, G. Behr, U. K. Rößler, K.-H. Müller, C. M. Schneider, and J. Schumann, J. Appl. Phys. **92**, 5413 (2002).
[25]K. Takakura, H. Ohyama, K. Takarabe, T. Suemasu, and F. Hasegawa, J. Appl. Phys. **97**, 093716 (2005).
[26]S. Y. Ji, J. F. Wang, J.-W. Lim, and M. Isshiki, Appl. Surf. Sci. **253**, 444 (2006).
[27]M. Uchikoshi, J. Imaizumi, H. Shibuya, T. Kékesi, K. Mimura, and M. Isshiki, Thin Solid Films **461**, 94 (2004).
[28]T. Kékesi, K. Mimura, and M. Isshiki, Hydrometallurgy **63**, 1 (2002).
[29]M. Takauji, N. Seki, T. Suemasu, F. Hasegawa, and M. Ichida, J. Appl. Phys. **96**, 2561 (2004).
[30]N. Hiroi, T. Suemasu, K. Takakura, N. Seki, and F. Hasegawa, Jpn. J. Appl. Phys., Part 2 **40**, L1008 (2001).
[31]J. E. Mahan, V. Le Thanh, J. Chevrier, I. Berbezier, J. Derrien, and R.G. Long, J. Appl. Phys. **74**, 1747 (1993).
[32]T. Miki, Y. Matsui, Y. Teraoka, Y. Ebina, K. Matsubara, and K. Kishimoto, J. Appl. Phys. **76**, 2097 (1994).
[33]I. Aksenov, H. Katsumata, Y. Makita, Y. Kimura, T. Shinzato, and K. Sato, J. Appl. Phys. **80**, 1678 (1996).
[34]K. Seeger, *Semiconductor Physics: An Introduction*, 6th ed. (Springer, Tokyo, 1997).
[35]J. D. Wiley and M. Didomenico, Jr., Phys. Rev. B **2**, 427 (1970).