Superconductivity in carrier-doped silicon carbide

To cite this article: Takahiro Muranaka et al 2008 Sci. Technol. Adv. Mater. 9 044204

View the article online for updates and enhancements.

Related content
- Superconductivity in heavily boron-doped silicon carbide
  Markus Kriener, Takahiro Muranaka, Junya Kato et al.
- Superconductivity in CVD diamond films
  Yoshihiko Takano
- Specific heat of aluminium-doped superconducting silicon carbide
  M Kriener, T Muranaka, Y Kikuchi et al.

Recent citations
- Superconductivity in nitrogen-doped 3C–SiC from first-principles calculations
  Ning Liu et al
- Infrared Spectroscopy and Structures of Boron-Doped Silicon Clusters (Si$_n$B$_m$, n = 3–8, m = 1–2)
  Nguyen Xuan Truong et al
- An improved genetic algorithm for crystal structure prediction
  S.Y. Chen et al
Superconductivity in carrier-doped silicon carbide

Takahiro Muranaka¹, Yoshitake Kikuchi¹, Taku Yoshizawa¹, Naoki Shirakawa² and Jun Akimitsu¹

¹ Department of Physics and Mathematics, Aoyama-Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan
² National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8578, Japan
E-mail: muranaka@phys.aoyama.ac.jp

Received 8 December 2008
Accepted for publication 12 December 2008
Published 28 January 2009

Abstract
We report growth and characterization of heavily boron-doped 3C-SiC and 6H-SiC and Al-doped 3C-SiC. Both 3C-SiC:B and 6H-SiC:B reveal type-I superconductivity with a critical temperature \( T_c = 1.5 \) K. On the other hand, Al-doped 3C-SiC (3C-SiC:Al) shows type-II superconductivity with \( T_c = 1.4 \) K. Both SiC:Al and SiC:B exhibit zero resistivity and diamagnetic susceptibility below \( T_c \) with effective hole-carrier concentration \( n \) higher than \( 10^{20} \) cm\(^{-3}\). We interpret the different superconducting behavior in carrier-doped \( p \)-type semiconductors SiC:Al, SiC:B, Si:B and C:B in terms of the different ionization energies of their acceptors.

Keywords: boron-doped SiC, Al-doped SiC, hexagonal and cubic SiC, type-I superconductor, type-II superconductor

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The recently discovered superconductivity in B-doped diamond (C:B) by Ekinov et al [1], subsequent enhancement of the critical temperature \( T_c \) in thin films to 11 K by Takano et al [2, 3], and observation of superconductivity in B-doped Si (Si:B) by Bustarret et al [4] have stimulated renewed interest in the low-carrier-density superconductivity of doped semiconductors. Many experimental and theoretical studies have focused on the origin of the metallic nature responsible for superconductivity in diamond. Investigations continue to clarify whether it originates from the holes at the top of the diamond valence band or from the boron impurity band formed above the valence band [5–15]. In particular, a higher-\( T_c \) superconductivity in C:B has been suggested from a theoretical model by a Japanese group [16–18], where bonds transform into bands by carrier doping of a semiconductor. In an extension of research on C:B and Si:B, our group focused on SiC. Silicon carbide has many stable polytypes, including cubic zinc-blende, hexagonal and rhombohedral polytypes. In the cubic zinc-blende structure, labeled as 3C-SiC or \( \beta \)-SiC, Si and C occupy ordered sites in a diamond framework. In hexagonal polytypes nH-SiC and rhombohedral polytypes \( nR \)-SiC, generally referred to as \( \alpha \)-SiC, \( nSi-C \) bilayers consisting of C and Si layers stack in the primitive unit cell. The lattice structures of the 3C-SiC and 6H-SiC phases, which are most important for this paper, are presented in figure 1.

Undoped SiC is a wide-band-gap semiconductor with a band gap of \( \sim 2–3 \) eV depending on the crystal modification. By carrier doping, we successfully induced type-I superconductivity in boron-doped SiC (SiC:B) with a boron doping level of \( \sim 1.06–1.91 \times 10^{21} \) cm\(^{-3}\) [19]. In the previously studied samples [19], both 3C-SiC:B and 6H-SiC:B phases were identified by powder x-ray diffraction (PXRD), and thus it was unclear which phase was superconducting.

SiC opens a new gateway to the physics of the new fascinating family of superconductors originating...
from wide-gap semiconductors. SiC lightly doped with donors or acceptors was intensively studied for N, P, B, Al, etc., introduced by ion implantation or thermal diffusion. A natural question arises whether SiC exhibits superconductivity when doped by other elements. In semiconductors, an insulator-to-metal transition takes place when the dopant-induced carrier concentration increases a certain level. Moreover, superconductivity has been experimentally achieved in some semiconductors at very low temperatures [21–24] following the theoretical predictions by Gurevich et al [25] and Cohen [26]. Recently, the semiconductor-to-metal transition has been realized in n-type N-doped 4H-SiC with carrier concentration above $10^{19}$ cm$^{-3}$ but without a report of superconductivity [27]; whereas p-type Al-doped 4H-SiC with Al concentration $n_{\text{Al}} = 8.7 \times 10^{20}$ cm$^{-3}$ showed metallic behavior and a small drop around 7 K in the temperature dependence of sheet resistance [28]. The authors mention that this drop may indicate the onset of a superconducting transition.

Here, we report superconductivity of B-doped 3C-SiC and 6H-SiC polytypes and of Al-doped 3C-SiC. Furthermore, we show that the superconductivity in hole-doped semiconductors can be interpreted in terms of the ionization energies of their acceptors.

2. Experimental details

Samples were prepared by substitutional reaction sintering from submicron 3C-SiC ($\beta$ form) powder (WAKO, mean particle size 0.27 $\mu$m), 6H-SiC ($\alpha$ form) powder (99%, RARE METALLIC), Si powder (99.99%), amorphous boron (99%), and Al powder (99.99%). The powders were mixed in certain proportions (typically SiC/Si/B or SiC/Si/Al with molar ratios 4:1:0.3–1.0), ground thoroughly, and pressed into pellets. They were then placed in an alumina boat and sintered in a pre-evacuated tube furnace at about 1600 $^\circ$C for 12 h, with heating and cooling rates of 200 $^\circ$C per hour, in a flow of Ar/H$_2$ gas mixture (50 ml/50 ml per minute). We have avoided the phase transition from 3C-SiC to 6H-SiC during the sintering, which occurs above 1700 $^\circ$C [29]. The as-prepared samples were cut into slices and the surface layers were removed before the transport measurements. An electron-probe microanalyzer with a wavelength-dispersive spectrometer (EPMA-WDS, JEOL, JXA-8200S) was employed for a quantitative elemental analysis. PXRD patterns were collected with CuK$\alpha$ radiation, using a conventional x-ray spectrometer equipped with a graphite monochromator (MultiFlex, RIGAKU), in the range 5° $\leq \theta \leq 80°$ at 0.02° step. For dc magnetic susceptibility and magnetization measurements in the temperature range 0.45–1.8 K, we employed a commercial SQUID magnetometer (MPMSR2 Quantum Design Co, Ltd) with a l-Helium$^3$He refrigerator. Electrical resistivity was measured with a conventional four-probe technique. The Hall coefficient was measured using a commercial system (PPMS Quantum Design Co, Ltd) in a five-probe ac mode, scanning the magnetic field from −5 to 5 tesla.

3. Superconductivity in B-doped SiC

The sintered 3C-SiC:B and 6H-SiC:B samples had black ceramic-like appearance. From typical PXRD patterns, the main phases in the 3C-SiC:B and 6H-SiC:B samples are indexed as the cubic zinc-blende 3C-SiC and the hexagonal 6H-SiC phases, respectively. In each sample, unreacted Si is detected. For the major 3C-SiC phase, the refined lattice parameter $a$ increased after sintering, but only by $\sim$0.1% from 4.3575(3) to 4.3618(4) Å. For the major 6H-SiC phase, the refined lattice parameter $c$ also increased after sintering by $\sim$0.2% from 15.06 to 15.09 Å. On the other hand, the refined lattice parameter $a$ did not change within the experimental accuracy. Note that the lattice parameter $a$ of commercial 6H-SiC is 3.064 Å. We expect that the presence of liquid silicon facilitates the boron diffusion, due to the much faster mass transport compared to the solid sintering, and enhances the boron substitution efficiency. The lattice parameter of silicon did not change after the sintering, indicating that little boron was doped into silicon.

The atomic sizes of boron and carbon are comparable, but are much smaller than that of silicon. Therefore, the minute change of the lattice parameters suggests that boron substitutes at the carbon site in these samples. We expect the boron substitution to be enhanced with a slow growth of crystal grains, and indeed, by the present synthetic method, the samples had much higher boron doping levels compared to the previous reports [30–33]. EPMA analysis with area-scans (within $50 \times 50 \mu$m$^2$) at various positions occasionally detected less than 0.05 at.% of Fe, together with Si, C and B, but no other elements, in all samples. From Hall measurements at room temperature, the effective hole concentrations $n$ are deduced as $\sim 1.91 \times 10^{21}$ cm$^{-3}$ for 3C-SiC:B and $\sim 2.53 \times 10^{20}$ cm$^{-3}$ for 6H-SiC:B.

As shown in figure 2, the magnetic susceptibility of 3C-SiC:B and 6H-SiC:B in a magnetic field of 1 Oe (zero field cooling process) significantly decreases at $\sim 1.4$ K, suggesting the occurrence of superconductivity. The estimated superconducting volume fraction at 0.45 K exceeds 100% because of the shielding effect. Figure 3 shows magnetization dependences versus magnetic field ($M$–$H$) of 3C-SiC:B and 6H-SiC, exhibiting the type-I superconducting behavior. In

![Figure 1](image-url). (a) Unit cell of cubic 3C-SiC. (b) Four unit cells of hexagonal 6H–SiC. For the drawings the software Vesta was used [20].
both compounds, the onset field of magnetization shows a hysteresis with about 30 Oe width at the lowest temperature. From the $M$–$H$ curves, we estimate the critical field $H_c$ as 100 Oe. The hysteresis width and $H_c$ value are consistent with the previous report on SiC:B [19].

Figure 4 presents the temperature dependence of the electrical resistivity in 3C-SiC:B and 6H-SiC:B. Both samples show metallic conductivity reflecting the high doping level. However, 3C-SiC:B exhibits a much smaller resistivity and almost linear temperature dependence at high temperatures due to the even higher boron doping concentration. The slope $d\rho/dT$ is always positive and its temperature dependence is linear for 3C-SiC:B, whereas a broad feature is observed at around 150 K for 6H-SiC:B suggesting a weak carrier localization or a contribution from non-metallic grain boundaries. The residual resistivity ratio $RRR (\rho_{300K}/\rho_{5K})$ is 11.4 and 4.7 for 3C-SiC:B and 6H-SiC:B, respectively. The inset of figure 4 shows an expanded view of the low-temperature data. Below 1.5 K (3C-SiC:B) and 1.4 K (6H-SiC:B), the resistivity drop indicates a clear superconducting transition and corresponds to the transition temperature observed in the magnetic susceptibility measurements. We note that despite the large difference in the residual resistivity, $T_c$ is nearly the same and the transition width is less than 0.2 K for both samples.

The phase diagram in the magnetic field–temperature ($H$–$T$) plane for both samples was determined using resistivity measurements. They involved varying the temperature (heating and cooling) at different magnetic fields ($T$-scan in figure 5), and varying the magnetic fields (increasing and decreasing) at different temperatures ($H$-scan in figure 6). The measurements were performed upon cooling and warming at constant magnetic field (0–80 Oe with a step 20 Oe) as well as upon increasing or decreasing the magnetic field (0–200 Oe) at constant temperature (0.35–1.0 K).

The temperature dependence of the in-field resistivity was measured as follows: the temperature was set above $T_c$. It was then reduced down to 350 mK (‘field-cooling (FC) run’) and subsequently increased above $T_c$ (‘warming after FC run’). Figure 5 shows the resistivity for $H = 0, 20, 40, 60$ and 80 Oe. In zero field, only one transition is found at $T_c$, whereas in finite fields, a large supercooling effect is observed in both SiC polytypes. We obtained the same curves independent of the chosen sweep rate, which guarantees that the observed supercooling behavior is an intrinsic property of the sample and that the superconducting transition in both polytypes is of the first order under finite fields. As shown in figure 6, the hysteresis was also observed in the magnetic field dependence of the resistivity. Above 130 Oe in 3C-SiC:B and above 120 Oe in 6H-SiC:B, we did not find any sign of superconductivity. The observations of the (i) in-field hysteresis, (ii) absence of a hysteresis in a zero field, and (iii) very small value of the critical field give strong evidence for type-I superconductivity in both SiC polytypes.

![Figure 2](image1.png)

**Figure 2.** Temperature dependence of dc magnetic susceptibility in 3C-SiC:B and 6H-SiC.

![Figure 3](image2.png)

**Figure 3.** Magnetization versus magnetic field in (a) 3C-SiC:B and (b) 6H-SiC.
supercooling) with an estimated \( H_{sc}(0) = (102 \pm 6) \text{ Oe} \) for 3C-SiC:B and \((94 \pm 3) \text{ Oe} \) for 6H-SiC:B, respectively.

Applying the Ginzburg–Landau (GL) theory of type-I superconductivity to these data, one can estimate an upper limit of the GL parameter \( \kappa \) from the difference of the critical fields obtained by a field-cooling run and a subsequent warming run \([34, 35]\): \( \kappa(0) \leq H_{sc}(0)/(1.695\sqrt{H_c}(0)) \). This yields \( \kappa \sim 0.32 \) for 3C-SiC:B and 0.31 for 6H-SiC:B, in agreement with the analysis of the Hall effect and the specific heat data given above, and therefore supports the type-I nature of superconductivity in SiC:B. Note that the value of \( \kappa \) is below 0.41, which is required in a model based on supercooling instead of superheating \([35–37]\).

### 4. Superconductivity in Al-doped SiC

The sintered 3C-SiC:Al sample had black ceramic-like appearance. From a typical PXRD pattern, three phases including 3C-SiC, unreacted Si and Al were identified. The main phase in 3C-SiC:Al sample is indexed as the cubic zinc-blende 3C-SiC. For the main phase 3C-SiC, the refined lattice parameter \( a \) increased after sintering by \( \sim 0.1\% \) from 4.338(5) to 4.342(4) \( \text{Å} \). Because the atomic sizes of Al and Si are comparable, but are much bigger than the atomic size of C, the minute change of the lattice parameters suggests that Al substitutes Si sites in 3C-SiC. The lattice parameter of Si did not change within the experimental resolution, indicating that little Al was doped into Si. We expect that the presence of liquid Si facilitates the Al diffusion due to the much faster mass transport compared to solid sintering, and enhances the Al-substitution efficiency. This also enhances the C site substitution by Si. EPMA analysis with area-scans (within 50 \( \times \) 50 \( \mu \text{m}^2 \)) at various positions detected Si, C and Al and no other elements. From room-temperature Hall measurements, the effective hole concentration was deduced as \( n \sim (3.86–7.06) \times 10^{20} \text{ cm}^{-3} \).

![Figure 4](image-url)  
**Figure 4.** Temperature dependence of resistivity in 3C-SiC:B and 6H-SiC:B. The inset magnifies the region near \( T_c \).

![Figure 5](image-url)  
**Figure 5.** Temperature dependence of resistivity under different magnetic fields (T-scan) in (a) 3C-SiC:B and (b) 6H-SiC:B.
As shown in figure 8, the magnetic susceptibility of SiC:Al in a magnetic field of 1 Oe (zero field cooling process) significantly decreases at 1.4 K, suggesting the occurrence of superconductivity. The estimated superconducting volume fraction at 0.45 K exceeds 100% because of the shielding effect. The inset of figure 8 shows magnetization versus magnetic field ($M$–$H$) curves, which are typical for a type-II superconductor. These $M$–$H$ curves and the value of $T_c$ exclude a possibility that superconductivity is caused by an impurity, such as Al ($T_c = 1.175$ K). From the $M$–$H$ curves, we estimate the lower critical field $H_{c1}$ as 53 Oe.

In figure 9, the resistivity of 3C-SiC:Al in zero magnetic field shows metallic behavior from room temperature, reflecting the high level carrier doping and a sharp drop at 1.5 K and zero resistivity below 1.35 K (inset in figure 9). The residual resistivity ($\rho_0$) and the residual resistivity ratio ($RRR$) are 0.746 m$\Omega$ cm and 5.3, respectively. The $\rho_0$ value is higher and the $RRR$ value is lower than those of 3C-SiC:B (60 $\mu\Omega$ cm and 10) [19], but the small transition width ($< 0.15$ K) reveals good quality of superconducting transition in SiC:Al. Among our samples sintered with other nominal compositions, $\rho_0$ and $RRR$ showed minor changes, however, the $T_c$ did not vary. The phase diagram in the magnetic field-temperature ($H$–$T$) plane was deduced from resistivity measurements. They involved varying the temperature (heating and cooling) at different magnetic fields ($T$-scan in figure 10(a)), and increasing and decreasing the magnetic fields at different temperatures ($H$-scan in figure 10(b)). Neither hysteresis nor supercooling behavior were observed in $T$-scan and $H$-scan, which is consistent with the transition to superconductivity under magnetic fields being of second order. Thus, a type-II superconductivity occurs in 3C-SiC:Al, in contrast with the
Figure 8. Temperature dependence of dc magnetic susceptibility in SiC:Al. The inset shows magnetization versus magnetic field at $T = 0.45$ K.

type-I superconductivity in 3C-SiC:B. Figure 11 presents the $T_c$ and the upper critical field $H_{c2}$, determined from the onset of resistivity, and the irreversibility field $H_{irr}$, determined from zero resistivity. Applying the conventional formula $H_{c2}(T) = H_{c2}(0)[1 - (T/T_c)^2]$, we plot the dependences $H_{c2}(T)$ with $H_{c2}(0) = 370 \pm 3$ Oe and the $H_{irr}(T)$ with $H_{irr}(0) = 140 \pm 4$ Oe.

Table 1 lists preliminary specific heat coefficients $\gamma_n$ [38]; basic normal-state parameters: Fermi wave number $k_F$, effective mass $m^*$, Fermi velocity $v_F$, mean free path $l$, as well as superconducting state parameters: penetration depth $\lambda$, coherence length $\xi$ and Ginzburg–Landau parameter $\kappa_{GL}$. Those parameters were estimated as described in [39]. For comparison, the previously reported parameters for 3C-SiC:B, C:B and Si:B are added. A small but larger than $1/\sqrt{2}$ value of $\kappa_{GL} \sim 1.8$ gives an evidence for type-II superconductivity.

Figure 9. Temperature dependence of resistivity in 3C-SiC:Al. The inset magnifies the region near $T_c$.

Our results also imply that 3C-SiC:Al, similar to SiC:B, is a dirty-limit superconductor because $\xi(0) \gg l$.

5. Discussion

Here, we introduce the ionization energies $E_A$ of the acceptors for qualitative understanding of superconductivity in doped semiconductors. Theoretically, the superconductivity in doped semiconductors can be interpreted in terms of degree of randomness caused by the impurity band, which is related to $E_A$ [17, 18, 42]. When $E_A$ is large (acceptor level is deep), the randomness caused by the impurity band is large. The $E_A$ values in $p$-type semiconductors [40, 41, 43] are shown.

Figure 10. (a) Temperature dependence of resistivity normalized by $\rho_0$ at different applied magnetic fields (0–400 Oe with a 20 Oe step) at 0.35–2 K ($T$-scan). (b) Magnetic field dependence of resistivity normalized by $\rho_0$ (0.35–1.0 K) at 0–400 Oe ($H$-scan).
in Table 2. The $E_A$ of 3C-SiC:Al is almost same with that of 3C-SiC:B (type-I superconductor) and smaller than that of C:B (type-II). Type-II superconductivity in C:B reveals carrier localization before the superconducting transition [1–3], and $\xi$ may be reduced by randomness caused by the dopant (80 nm). On the other hand, type-I superconductivity of 3C-SiC:B does not reveal such carrier localization [38], and $\xi$ is not reduced by randomness ($\xi \sim 360$ nm). Superconductivity in SiC:Al does not reveal carrier localization, similar to SiC:B, and the $\kappa_{GL}$ value is small ($\sim 1.8$), but larger than $1/\sqrt{2}$. Therefore, from $E_A$ value, we consider that the superconductivity in 3C-SiC:Al is at the border between type I and type II.

In terms of $E_A$, Si:B must reveal type-I superconductivity because $E_A$ has the smallest and its randomness due to the dopant must be small, according to theory. In the previous report by Bustarret et al [4], B was introduced to Si thin films using UV laser doping technique. Such B-doped Si thin films may include defects or disorder. Because type-I superconductivity can be hidden and change to type-II behavior by disorder or impurities, type-II superconductivity in Si:B might be influenced by the crystal defects or disorder. From the same point of view, type-II superconductivity in SiC:Al with a small $\kappa_{GL}$ value may be essentially a type-I superconductivity hidden by crystal defects or impurities. In preliminary ac susceptibility results ($T$-scan and $H$-scan), small hysteresis between cooling and warming process was observed ($\Delta T \sim 0.02$ K at $H = 100$ Oe, $\Delta H \sim 19$ Oe at $T = 0.26$ K) [38]. Concentration of crystal defects and impurities should be reduced in SiC:Al for a more detailed study of the superconductivity.

6. Summary

We successfully synthesized boron-doped SiC (3C- and 6H-SiC polytypes) and Al-doped 3C-SiC by a substitutional sintering method and characterized bulk superconductivity in those materials. Both 3C-SiC:B and 6H-SiC:B reveal type-I superconductivity at $T_c = 1.5$ K. On the other hand, Al-doped 3C-SiC (3C-SiC:Al) reveals type-II superconductivity at $T_c = 1.4$ K. Using this observation, the superconductivity in carrier-doped semiconductors can be interpreted in terms of the depth of acceptor levels in $p$-type semiconductors. One may only speculate on the physical reasons behind this difference. One possibility could be a much different Fermi velocity $v_F$ in the case of SiC:B due to a different shape of the Fermi surface. Further experimental and theoretical work is clearly required.
Acknowledgments

We would like to acknowledge Dr M Kriener, Professor Y Maeno (Kyoto University) and Dr Y Yanase (Tokyo University) for helpful discussions. This work was supported by ‘High-Tech Research Center’ Project for Private Universities from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Grant-in-Aid for Young Scientists (B) (No. 20740202) and a Grand-in-Aid for Scientific Research on Priority Area (no. 16076212) from MEXT.

References

[26] Cohen M L 1964 Rev. Mod. Phys. 36 240