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Superconductivity in compensated and uncompensated semiconductors

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Abstract

We investigate the localization and superconductivity in heavily doped semiconductors. The crossover from the superconductivity in the host band to that in the impurity band is described on the basis of the disordered three-dimensional attractive Hubbard model for binary alloys. The microscopic inhomogeneity and the thermal superconducting fluctuation are taken into account using the self-consistent 1-loop order theory. The superconductor-insulator transition accompanies the crossover from the host band to the impurity band. We point out an enhancement of the critical temperature T_c around the crossover. Further localization of electron wave functions leads to the localization of Cooper pairs and induces the pseudogap. We find that both the doping compensation by additional donors and the carrier increase by additional acceptors suppress the superconductivity. A theoretical interpretation is proposed for the superconductivity in the boron-doped diamond, SiC, and Si.

Keywords: superconductivity, semiconductor, localization, diamond

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

1. Introduction

Superconductivity in the vicinity of the quantum phase transition has attracted much interest. High-T_c cuprates [1], organic superconductors ([2] and references therein), and heavy fermion superconductors (for a review see [3]) in proximity to various quantum critical points have been a central field of the condensed matter physics. Another classical issue is the superconductor–insulator transition which arises from the competition between the Anderson localization [4] and the *s*-wave superconductivity. Many theoretical studies have been devoted to the superconductor–insulator transition triggered by disorder [5–13], ([14] and references therein), [15, 16]. In this paper, we point out that the recently discovered superconductivity in boron-doped diamond [17] and related materials [18–20] provide a new field of the superconductivity in the vicinity of the Anderson localization.

Diamond is an insulator, which becomes a semiconductor by moderate boron doping. Superconductivity in diamond has been discovered by Ekimov *et al* by increasing the boron concentration [17]. The transition temperature of 11.4 K has been realized in heavily B-doped diamond [21, 22]. It is surprising that such a high transition temperature is induced by the low carrier concentrations in a three-dimensional system because small density of states (DOS) near the band edge is detrimental for the superconductivity. A novel mechanism is expected for the enhancement of superconductivity in the B-doped diamond.

Two theoretical scenarios have been proposed for the superconductivity in B-doped diamond. First one is based on the impurity band formed by the impurity states localized around boron atoms[1] [24, 25]. It was proposed by Baskaran [24] just after the discovery of superconductivity, and has been described by Shirakawa *et al* on the basis of the coherent potential approximation [25]. The other model is based on the host band of diamond in which the carriers are provided by substitutional boron acceptors; it has been supported by first-principle band calculations [26–29].

Experimental studies have examined which scenario describes better the electronic structure of B-doped diamond [30–37]. We point out here that the two scenarios

[1] The superconductivity in the impurity band has been proposed in 80s for Si:Au.

are not contradictory and can be described continuously. It is important to note that the localization effects have not been investigated in the theories on the B-doped diamond [24–29], although localization plays essential role in semiconductors. Actually, semiconductors have been a central field for the experimental study on the Anderson localization [38–40].

We have previously demonstrated that the Anderson localization occurs in the crossover region [41]. Here we show that the Anderson localization is accompanied by the enhancement of Cooper pairing, localization of Cooper pairs, and the pseudogap. The effect of doping on the superconductivity and pseudogap is also investigated.

Boron doping leads to the superconductivity not only in diamond, but also in Si [18] and SiC [19]. Recently, superconductivity has been realized in the Al-doped SiC [20]. Here we propose a theoretical interpretation for the differences between these superconductors.

2. Model

For the discussion of superconductivity in doped semiconductors, we investigate the disordered attractive Hubbard model in three dimensions

$$H = -t \sum_{\langle i,j\rangle,\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{i} (W_i - \mu) n_i + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}, \quad (1)$$

where $n_{i,\sigma}$ is the electron number at the site i with the spin σ, and $n_i = \Sigma_\sigma n_{i,\sigma}$. The symbol $\langle i, j\rangle$ denotes the summation over the nearest neighbor sites. The last term describes the attractive interaction $U < 0$. Simple cubic lattice is assumed. We choose the energy units of $t = 1$.

The disorder is described by the random potential W_i. We assume a binary alloy model in which $W_i = 0$ at host sites (carbon sites in the B-doped diamond) and $W_i = U_{\rm imp}$ at impurity sites (boron sites in the B-doped diamond). We denote the impurity concentration as $n_{\rm imp}$ and describe the total electron concentration as $n = 2 - n_{\rm c}$. Note that $n_{\rm c} = n_{\rm imp}$ in the uncompensated semiconductors. Doping compensation by donors and carrier increase due to additional acceptors lead to $n_{\rm c} < n_{\rm imp}$ and $n_{\rm c} > n_{\rm imp}$, respectively. We first describe the global phase diagram for the uncompensated semiconductors in section 3.2 and investigate the doping dependence in section 3.3. The effects of doping compensation and carrier increase are examined in section 3.4. Note that presence of B–H complex [43] is not regarded as compensation. The impurity concentration $n_{\rm imp}$ does not correspond to the concentration of boron atoms, but describes the number of impurity states around the isolated boron atoms. Actually, the electronic state around the B–H complex is negligible for the superconductivity.

3. Superconductivity

3.1. Formulation

We analyze the model of equation (1) on the basis of the real-space self-consistent T-matrix approximation (RSTA) which has been formulated to investigate the disordered d-wave superconductivity [44]. The calculation is carried out above $T_{\rm c}$, and the instability to the superconducting transition is investigated. The thermal fluctuation of superconductivity is taken into account in the self-consistent 1-loop order. Although the fluctuation has been neglected in many microscopic investigations of the random systems [45–47], it plays an essential role in strongly disordered systems because the microscopic inhomogeneity enhances the fluctuations [10, 44].

The correlation function of the superconductivity $T(\vec{r}, \vec{r'}) = \int_0^\beta \langle \Delta(\vec{r}, \tau)\Delta(\vec{r'}, 0)\rangle \, {\rm d}\tau$ and the single-particle Green function $G(\vec{r}, \vec{r'}, \omega_n)$ are self-consistently determined for each impurity distribution. Taking the random average, the averaged correlation function $T_{\rm av}(\vec{r}) = \langle T(\vec{r} + \vec{r'}, \vec{r'})\rangle_{\rm av}$ and the averaged Green function $G_{\rm av}(\vec{r}, \omega_n) = \langle G(\vec{r} + \vec{r'}, \vec{r'}, \omega_n)\rangle_{\rm av}$ are obtained. The averaged superconducting susceptibility and the single-particle DOS are obtained as

$$\chi_{\rm sc} = \sum_{\vec{r}} T_{\rm av}(\vec{r}) \quad (2)$$

and

$$\rho(\omega) = -\frac{1}{\pi} {\rm Im}\, G^{\rm R}_{\rm av}(0, \omega), \quad (3)$$

respectively.

We show the calculation results on the $11 \times 11 \times 11$ lattice, unless mentioned otherwise. This size is much larger than the limit of quantum [14] and classical [15] Monte Carlo simulations. The expression of the RSTA is shown in [48]. The validity of the self-consistent 1-loop approximation has been examined in the clean limit [49].

The randomness is accurately taken into account in the RSTA. The spatial dependences of the superconducting fluctuation and single-particle states are self-consistently determined. We find that the perturbative approximations for the impurity potential, such as the Born approximation [50], coherent potential approximation [25], and T-matrix approximation [51], break down for a large impurity potential $U_{\rm imp} > 4$. This is because the quasiparticles around the Fermi level mainly consist of the impurity states whose wave function is spatially localized around the boron sites. The impurity potential should be taken into account in the zero-order approximation when the impurity sites play a major role for the superconductivity.

3.2. Crossover from host band to impurity band

The crossover from the host band to the impurity band is described by varying the impurity potential $U_{\rm imp}$ in the model of equation (1). Figure 1 shows the DOS for various impurity potentials $U_{\rm imp}$.

For a large impurity potential $U_{\rm imp} = 6.1$, the impurity band is clearly separated from the host band, as shown in figure 1(d). The holes are nearly half-filled in the impurity band when the acceptors are uncompensated, $n_{\rm c} = n_{\rm imp}$. For a small impurity potential $U_{\rm imp} = 3$, the impurity band is implanted into the host band, as shown in figure 1(a). The single-particle states around the Fermi level are formed by the impurity states localized around the boron atoms for $U_{\rm imp} = 6.1$, while the low-energy states are basically

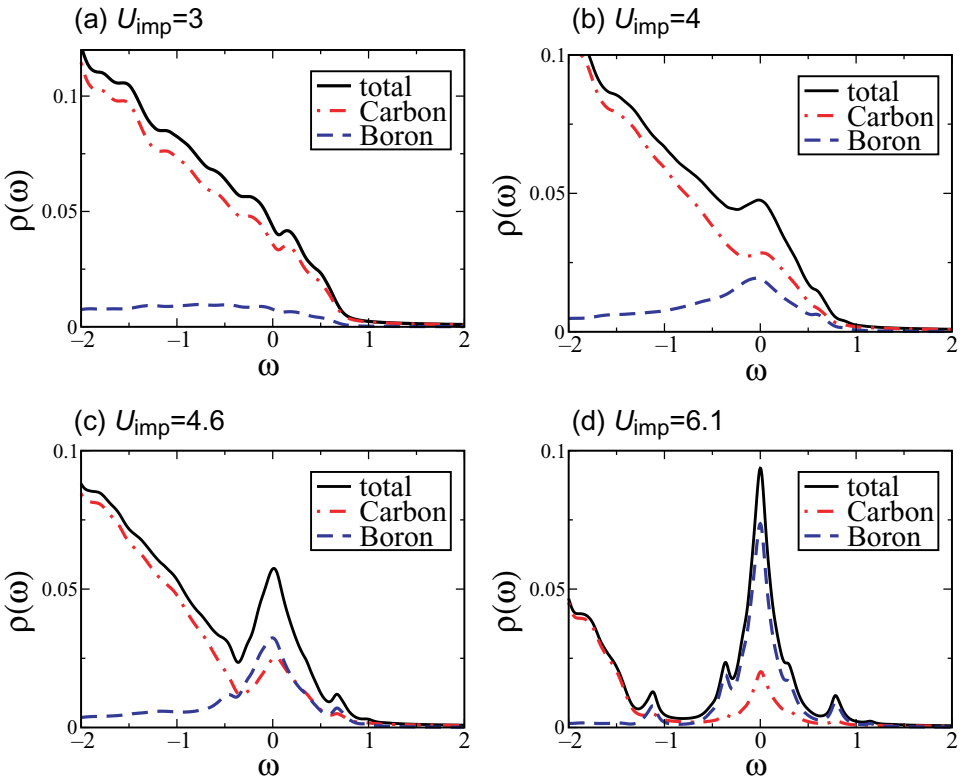

Figure 1. DOS in the normal state (solid line). We assume $n_c = n_{imp} = 0.02$ and $U = 0$. The dashed (dash-dotted) line shows the partial DOS at the boron (carbon) sites. The calculation is carried out on 21^3 sites and 50 samples are taken for the random average.

described by the host band for $U_{imp} = 3$. The crossover between these two regimes occurs around $U_{imp} = 4$–4.6. It is shown that the impurity band merges with the host band upon decreasing U_{imp} (See figures 1(b) and (c)). The acceptor level of the lightly boron-doped diamond is 0.37 eV [52], which corresponds to $U_{imp} \sim 4.6$ [25]. This implies that the B-doped diamond is in the crossover regime between the host band and the impurity band. The crossover from the impurity band to the host band occurs also by increasing the doping concentration n_{imp}.

We summarize here our results of superconductivity in the uncompensated semiconductors [48]. Figure 2 illustrates the schematic phase diagram of the impurity potential U_{imp} and temperature T for a fixed impurity concentration $n_{imp} = n_c$.

The Cooper pairing is enhanced in the crossover region because the pairing interaction is effectively enhanced by the localization of single-particle wave functions [13]. The crossover from the wide host band to the narrow impurity band is accompanied by the decrease of the Fermi energy E_F, and leads to the increase of the ratio $|U|/E_F$. Therefore, the transition temperature T_c^{MF} in the mean field theory and the magnitude of the superconducting gap monotonically increase by increasing the impurity potential U_{imp} (dashed line in figure 2). We have confirmed this U_{imp} dependence of the superconducting gap in the mean field theory at $T = 0$ [53].

The Anderson localization of the single-particle wave function leads to the microscopic inhomogeneity of the superconductivity. Figure 3 shows the spatial dependence of

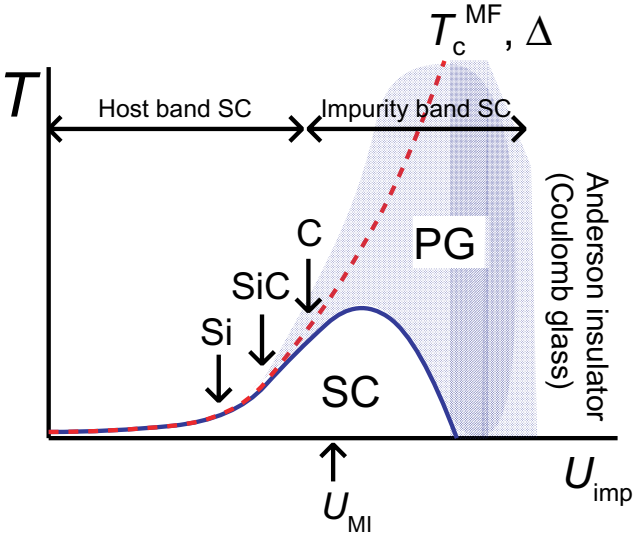

Figure 2. Schematic phase diagram of the uncompensated semiconductors describing the crossover from the host band to the impurity band. The solid line shows the transition temperature of superconductivity, T_c. The dashed line shows the transition temperature in the mean field theory, T_c^{MF}. The shaded region indicates the pseudogap state induced by the incoherent Cooper pairs. The up arrow (U_{MI}) shows the virtual quantum metal–insulator transition in absence of the superconductivity. Down arrows indicate our interpretation on the B-doped diamond, SiC, and Si (see section 4).

the superconducting susceptibility $\chi_{sc}(\vec{r})$

$$\chi_{sc}(\vec{r}) = \sum_{\vec{r}'} T(\vec{r}, \vec{r}'), \tag{4}$$

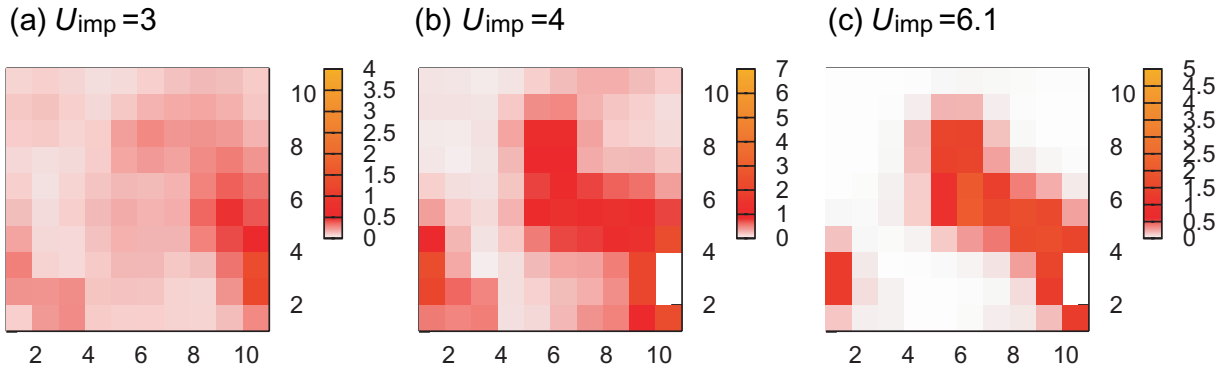

Figure 3. A typical spacial dependence of the superconducting susceptibility $\chi_{sc}(\vec{r})$ for (a) $U_{imp} = 3$, (b) $U_{imp} = 4.0$, and (c) $U_{imp} = 6.1$. We assume $n_c = n_{imp} = 0.02$, $T = 0.002$, and $U = -1$. The calculation is carried out in the $11 \times 11 \times 11$ lattice. The results on the 11×11 plane at $z = 1$ are shown.

for a typical distribution of impurities. We see that the inhomogeneity is enhanced by increasing the impurity potential and approaching the impurity band regime. In other words, the Cooper pairs are localized owing to the localization of single-particle wave functions. Then, the microscopic inhomogeneity enhances the fluctuation of superconductivity and disturbs the long-range coherence. The competition between the enhancement of the effective pairing interaction and that of the fluctuations leads to a dome shape of the superconducting state with a peak of T_c in the crossover regime, as shown in figure 2 (solid line).

The short-range correlation of superconductivity gives rise to the pseudogap above T_c in the shaded region of figure 2 (see figure 5). In other words, the superconducting gap obtained in the mean field theory is changed to the pseudogap by the fluctuations. The pseudogap state would be an insulating state in the highly disordered regime because both electrons and Cooper pairs are localized. This state is qualitatively the same as the 'hard gap insulator' proposed by Feigel'man *et al* [13] which seems to be realized in disordered thin films [54–63].

3.3. Doping dependence

We investigate here the doping dependence of the uncompensated system, where $n_c = n_{imp}$. The impurity level depends on the impurity concentration n_{imp}, but we fix here the impurity potential U_{imp} for simplicity. We focus on the crossover regime between the impurity band and the host band, which seems to be realized in the B-doped diamond, as will be discussed in section 4.

Figure 4 shows the doping dependence of the Fourier transformed correlation function,

$$T^{q}(\vec{q}) = \int T_{av}(\vec{r}) e^{i\vec{q}\vec{r}} \, d\vec{q}. \tag{5}$$

This correlation function at $\vec{q} = 0$ is divergent at the critical point. We see that the correlation function increases at $\vec{q} = 0$ upon increasing the doping concentration while that does not change so much at $\vec{q} \neq 0$. This means that the long-range correlation is enhanced by increasing the concentration of impurities. This is consistent with the experimental

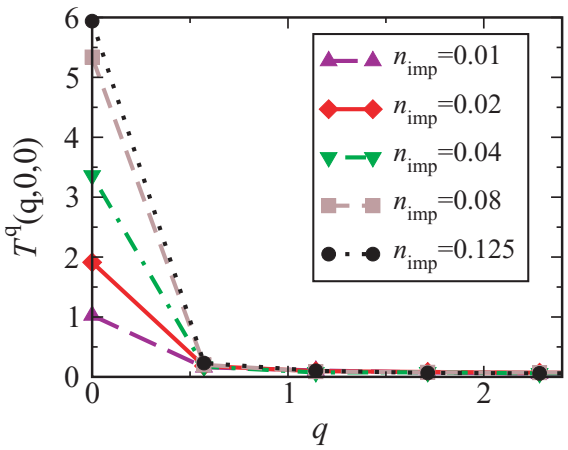

Figure 4. Doping dependence of the Fourier transformed correlation function $T^{q}(\vec{q})$ in the crossover regime. We show the $T^{q}(\vec{q})$ along $\vec{q} = q\hat{x}$ for $n_c = n_{imp} = 0.01, 0.02, 0.04, 0.08, 0.125$ from the bottom to the top. We fix $U_{imp} = 4.6$, $U = -1$, and $T = 0.002$.

observation that the T_c of B-doped diamond increases with increasing the boron concentration [21, 22, 32, 43]. Note that the impurity concentration n_{imp} in our definition corresponds to the concentration of isolated substitutional boron acceptors. It has been pointed out that the concentration of carries is different from that of boron atoms owing to the presence of B–H complex and/or B–B dimer and the superconducting T_c is determined by the concentration of carriers [43, 65]. We have confirmed that the B–H complex or B–B dimer neither enhance nor suppress the superconductivity [66]. Thus, our results on the doping dependence are consistent with the experiment [43].

Figure 5 shows the doping dependence of the DOS above T_c in the crossover regime. We see that the pseudogap is induced by the incoherent Cooper pairs. Doping suppresses the pseudogap although the superconducting correlation is enhanced, as shown in figure 4. This is because the Anderson localization is suppressed by the percolation of impurity states. The single-particle states become itinerant, and then the homogeneous superconducting correlation suppresses the superconducting fluctuation as well as the pseudogap. We confirmed that the transition temperature T_c^{MF} in the

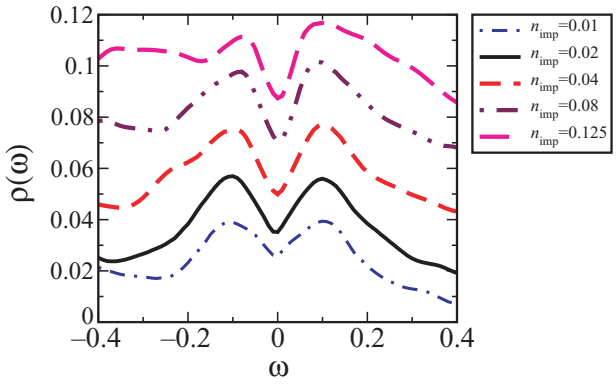

Figure 5. DOS for $n_c = n_{imp} = 0.01, 0.02, 0.04, 0.08, 0.125$ from the bottom to the top. We assume $U_{imp} = 4.6$, $U = -1$, and $T = 0.002$.

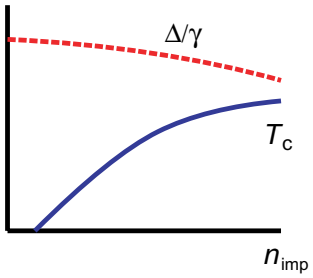

Figure 6. Schematic figure of the doping dependence in the crossover regime. We show the magnitude of the superconducting gap (pseudogap) Δ divided by $\gamma = 1.73$ for a comparison with the T_c.

mean field theory decreases with increasing the doping concentration in contrast to the T_c. This is also because the Anderson localization is suppressed by the doping.

On the basis of these results, we illustrate the schematic figure of the doping dependence in figure 6. Note again that the T_c of the superconductivity increases, but the thermal fluctuation is suppressed by increasing the doping concentration. The pseudogap and superconducting gap decrease, in contrast to the T_c, upon increasing the concentration of impurities. These doping dependences should be contrasted to those in the host band regime, where the thermal fluctuation is negligible except for a very small concentration of impurities. A usual doping dependence is expected in the host band region—the superconducting gap increases together with the T_c upon increasing the doping n_{imp}.

3.4. Effect of compensation

Here we examine the difference between the compensated and uncompensated semiconductors. Figure 7 shows the averaged superconducting susceptibility χ_{sc} for various carrier concentrations n_c with a fixed impurity concentration $n_{imp} = 0.02$. The superconducting susceptibility χ_{sc} shows a sharp maximum at $n_c = n_{imp}$ for $U_{imp} = 4.6$. This means that the superconductivity is stable in the uncompensated semiconductor rather than the compensated one. Both doping compensation ($n_c < n_{imp}$) and carrier increase ($n_c > n_{imp}$) suppress the superconductivity in the crossover and host band

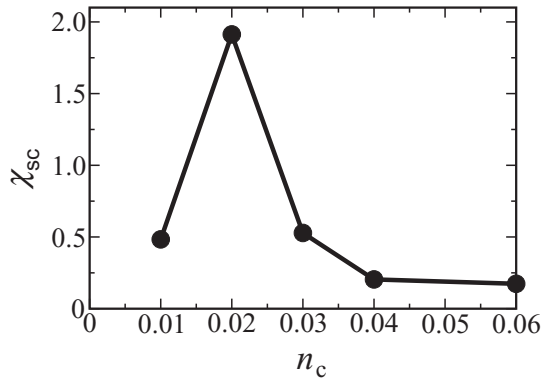

Figure 7. Averaged superconducting susceptibility for various carrier concentration n_c. The impurity concentration is fixed to be $n_{imp} = 0.02$. We assume $U_{imp} = 4.6$, $U = -1$, and $T = 0.002$.

regimes. This is because the DOS has a peak at $n_c = n_{imp}$ as shown in figures 1(b)–(d). Both doping compensation and carrier increase decrease the DOS at the Fermi level, and therefore the superconductivity is suppressed.

A qualitatively different carrier concentration dependence is expected in the host band regime. The instability to the superconductivity is determined by the number of carriers n_c and nearly independent of the impurity concentration n_{imp} for a small impurity potential $U_{imp} \ll 4$. Then, the T_c of superconductivity monotonically increases with increasing the carrier concentration n_c.

The carrier increase ($n_{imp} < n_c$) can be induced by additional acceptors with a small U_{imp}. When the impurity potential U_{imp} of those additional acceptors is much smaller than that of boron acceptors, we can ignore the former as we have done in this paper. If the carrier increase is experimentally realized, the carrier concentration dependence of T_c would be a crucial measurement to determine which is important for the superconductivity between the impurity band and host band.

4. Interpretation of superconductivity in B-doped diamond, SiC and Si

We discuss here the superconductivity in the B-doped diamond, SiC, and Si. Because the impurity band is not clearly observed in the angle resolved photo emission spectroscopy [33, 34], the B-doped diamond seems to be in the host band or crossover regime. On the other hand, a high transition temperature $T_c > 10\,\mathrm{K}$ [21, 22], high upper critical field $H_{c2} > 10\,\mathrm{T}$ [21, 22, 31], and a large Ginzburg–Landau parameter $\kappa \sim 18$ [31] imply that the B-doped diamond is close to, or in the crossover regime. In general, the localization of single-particle wave functions gives rise to the short coherence length and the small superfluid density. Therefore, the high upper critical field H_{c2} and large Ginzburg–Landau parameter κ are realized in the crossover regime. The localization effect revealed by the electric resistivity measurements [21, 30] also indicates that the B-doped diamond is close to the crossover regime.

These observations should be contrasted to the B-doped SiC. The B-doped SiC is a type I superconductor in which

the critical field H_c is 1000 times smaller than in B-doped diamond [19]. A small Ginzburg–Landau parameter $\kappa \sim 0.35$ [19, 42] has been reported. These marked differences between the diamond and SiC indicate that the B-doped SiC is in the host band regime far from the crossover. This is consistent with the boron acceptor level in SiC ~ 0.3 eV [20] ([67] and references therein) which is smaller than that in the diamond. Small residual resistivity also implies that the effect of the Anderson localization is negligible for the superconductivity in the B-doped SiC. It is expected that the B-doped Si is furthermore far from the crossover because the acceptor level $\sim$0.045 eV [20] ([68] and references therein) is the smallest among the B-doped diamond, SiC, and Si. We have illustrated these interpretations in figure 2.

We comment here on the difference between the B-doped and Al-doped SiC. Both compounds have a similar $T_c \sim 1.5$ K. However, the Al-doped SiC seems to be a type II superconductor with $\kappa \sim 1.8$ in contrast to the type I superconductivity in the B-doped SiC. Because the acceptor level of the Al-doped SiC ~ 0.2 eV [20] ([67] and references therein) is smaller than that of the B-doped SiC, these experimental observations seem to be incompatible with the interpretation based on figure 2. However, the difference between the B-doped and Al-doped SiC may be understood in the following way. We expect that the silicon sites play more important roles for the superconductivity than the carbon sites because the DOS at the Fermi level mainly arises from the silicon sites [20]. It has been pointed out that the boron atoms mainly substitute the carbon site [20], while the aluminum atoms substitute the silicon sites rather than the carbon sites. Therefore, the disordered potential due to the substitution of aluminum atoms affects the superconductivity more significantly than the boron substitution. Then, the type I superconductivity can occur in the B-doped SiC although the acceptor level is larger than that of the Al-doped SiC. Further experimental studies are desired to examine this possibility.

5. Summary and discussion

We have investigated the localization and superconductivity in doped semiconductors on the basis of the disordered attractive Hubbard model in three dimensions. We focused on the crossover from the superconductivity in the host band to that in the impurity band. We found that the effective pairing interaction is enhanced in the crossover regime where the metal–insulator transition occurs owing to the Anderson localization. The superconducting correlation is enhanced in the crossover regime, but suppressed by the mesoscopic and thermal fluctuations as approaching to the impurity band regime. The long-range coherence is destroyed in the impurity band regime, and then the short range correlation leads to the pseudogap. Finally, the insulating state due to the localization of Cooper pairs is realized in the highly disordered regime.

The marked differences between the B-doped diamond, SiC, and Si can be understood by taking into account their impurity potentials determined by the acceptor level in the lightly doped regime. The B-doped diamond seems to be close to or in the crossover regime, while Si and SiC are far away from the crossover regime. The experimental results on the transition temperature, critical field, residual resistivity, and the nature of the superconductor–insulator transition are consistent with our interpretation.

Finally, we point out the similarity between the superconductivity in the doped semiconductors, disordered thin films, and high-T_c cuprates. Presence of incoherent Cooper pairs has been indicated in the thin films [13, 16, 56–63] as well as in high-T_c cuprates [69–71]. The pseudogap of the excitation spectrum has been observed in both systems. We have pointed out that the doped wide-gap semiconductor would be a new family of the incoherent Cooper pairing state. The simple electronic structure of the doped semiconductors would accelerate the development of microscopic theories on the superconductor–insulator transition induced by the localization of Cooper pairs. Future experimental and theoretical efforts are highly desired to clarify novel superconducting properties in these systems.

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