Low-temperature conductivity of semiconductors doped heavily with nonhydrogenic impurities

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A theory of the conductivity in heavily doped semiconductors which has previously been developed for hydrogenic impurities is extended to the case of nonhydrogenic impurities. The effect of nonhydrogenic scattering behavior is taken into account semiempirically with the use of the experimental data of the binding energy of an isolated impurity. It is shown that the theory well explains experimental results of the dependence of the low-temperature conductivity of semiconductors where the impurity scattering is not hydrogenic.

I. INTRODUCTION

The low-temperature conductivity in heavily doped semiconductors is of academic interest because electrons interact strongly with many impurities simultaneously, as in the localization and delocalization problem. Although various theories[1-7] have been developed so far in order to understand the conduction in the presence of ionized impurities, they have turned out to be incapable of explaining[8,9] the conduction at high doping levels especially at low temperatures. In a previous paper[10] the present author has developed a theory of the conductivity at high doping levels which is based on the Green's function formalism using the bent-band model; the theory is named the bent-band theory. In this theory all the terms of the multisite multiple Born scatterings have been taken into account. It has turned out that the theory can explain experimental results much better than other theories. Nevertheless, the agreement between the theory and experiments is still unsatisfactory except the case of Ge:As. Especially the dependence of the conductivity on the impurity species of the same valence for a given host could not be explained by the bent-band theory.

Pantelides and Sah[11] (PS) have pointed out in their analysis of localized states that the binding energy of an impurity is well described by the effective-mass theory only for impurities having the same core as the host atoms; PS called such impurities "isocoric" impurities. PS have taken into account the core effect by using the pseudopotential, obtaining fruitful results.

The present paper describes the calculation of the conductivity which is carried out by taking into account the core effect of the impurities semiempirically. The theory is applied to n-type Ge, p-type Ge, and n-type Si for which the experimental data at sufficiently low temperature are available.

II. ANALYTICAL PROCEDURE

The expression for the conductivity σ at 0 K, which has been derived previously,[10] is as follows:

$$\sigma=\sigma_1+\sigma_2 , \tag{2.1}$$

$$\sigma_1=\frac{e^2}{\hbar}\frac{2\sqrt{2}}{3\pi^3}\left[\frac{\lambda}{a_B}\right]^{1/2}\frac{m_D}{m_C}\nu\int_{-\infty}^{\Omega_F}d\Omega(\Omega_F-\Omega)^{3/2}[\mathrm{Im}\bar{G}^{R}(\Omega)]^2 , \tag{2.2}$$

$$\sigma_2=\frac{e^2}{\hbar}\frac{\lambda}{6\pi^3}\frac{m_D}{m_C}\int_0^{x_c}dx\int_{-\infty}^{\Omega_F}d\Omega[\mathrm{Im}\bar{G}^{R}(\Omega,\beta_c;x)-\mathrm{Im}\bar{G}^{R}(\Omega,\beta_c;\infty)]$$
$$\times\left\{\frac{2}{x^2}\left[1-\cos\left[\frac{2k}{\lambda}x\right]\right]-\frac{4k}{x\lambda}\sin\left[\frac{2k}{\lambda}x\right]+\frac{2k^2}{\lambda^2}\left[1+\cos\left[\frac{2k}{\lambda}x\right]\right]\right\} . \tag{2.3}$$

In the above equations e is the electronic charge, $\hbar$ the Planck constant divided by 2π, m_C the conductivity mass, m_D the density-of-states mass, a_B the effective Bohr radius $\hbar^2\epsilon_0/(m_De^2)$ with ϵ_0 being the dielectric constant of the host lattice, ν the number of the valleys, λ the Thomas-Fermi inverse screening length, $\Omega_F=[\epsilon_0/(e^2\lambda)]\omega_F$ with ω_F being the Fermi level measured from the unperturbed band edge, $k^2=(2\lambda/a_B)(\Omega_F-\Omega)$, and x_c and β_c some constants discussed previously.[10] In Eq. (2.2) $\bar{G}^{R}(\Omega)$ is the one-particle retarded Green's function in a dimensionless form, i.e.,

$$\bar{G}^{R}(\Omega)=\frac{1}{j}\int_0^{\infty}d\xi\exp[j\xi\Omega+\gamma g(\xi)] , \tag{2.4}$$

where $j^2=-1$, $\gamma=4\pi n_i/\lambda^3$ with n_i being the impurity concentration assumed to be equal to the carrier concentration divided by $|Z|$, and

$$g(\xi)=\int_0^\infty dx\, x^2\left[\exp\left[-j\xi\frac{Z}{x}\exp(-x)\right]-1\right]+jZ\xi \tag{2.5}$$

with Z being the minus of the difference between the valencies of the impurity atom and the host atom. In Eq. (2.3) $\bar{G}^R(\Omega,\beta;x)$ coming from two-particle Green's function is given as

$$\bar{G}^R(\Omega,\beta;x)=\frac{1}{j}\int_0^\infty d\zeta\exp[j\zeta\Omega+\gamma\phi(\zeta,\beta)]\,, \tag{2.6}$$

where

$$\phi(\zeta,\beta)=jZ\zeta+P\left[\frac{\zeta+\beta}{2},\frac{\zeta-\beta}{2};x\right] \tag{2.7}$$

with

$$P(\xi,\eta;x)=\int d\mathbf{x}'\left[\exp\left[-j\xi\frac{Z}{|\mathbf{x}'-\frac{1}{2}\mathbf{x}|}\exp(-|\mathbf{x}'-\tfrac{1}{2}\mathbf{x}|)-j\eta\frac{Z}{|\mathbf{x}'+\frac{1}{2}\mathbf{x}|}\times\exp(-|\mathbf{x}'+\tfrac{1}{2}\mathbf{x}|)\right]-1\right]. \tag{2.8}$$

Here $\mathbf{x}'$ and $\mathbf{x}$ are the three-dimensional position vectors given in dimensionless forms with $x=|\mathbf{x}|$. In giving the expression for σ, we have considered in general multivalley semiconductors with ellipsoidal energy surfaces characterized by the longitudinal effective mass $m_\parallel$ and the transverse effective mass $m_\perp$ as in the case of Ge and Si. Then we have $m_C^{-1}=(m_\parallel^{-1}+2m_\perp^{-1})/3$ and $m_D=(m_\parallel m_\perp^2)^{1/3}$. The density-of-states mass m_D is defined by expressing the density of states as a function of energy. In this view we also define m_D for the valence band so that for this band we use Eqs. (2.2) and (2.3) and the equations that will follow.

The Fermi level ω_F is determined from

$$n_i=\int_{-\infty}^{\omega_F}d\omega\,\rho(\omega)\,, \tag{2.9}$$

where the density of states $\rho(\omega)$ is given as

$$\rho(\omega)=-\frac{\sqrt{2}}{\pi^3}\left[\frac{\epsilon_0}{e^2\lambda}\right]^2\left[\frac{\lambda}{a_B}\right]^{3/2}\nu\times\int_{-\infty}^{\Omega_\omega}d\Omega(\Omega_\omega-\Omega)^{1/2}\mathrm{Im}\bar{G}^R(\Omega) \tag{2.10}$$

with $\Omega_\omega=[\epsilon_0/(e^2\lambda)]\omega$; ω is the energy measured from the unperturbed band edge. The inverse screening length λ, which has appeared in all the above equations, is given by

$$\lambda^2=\frac{8\sqrt{2}}{\pi^2}\left[\frac{\lambda}{a_B}\right]^{3/2}\frac{\nu}{\lambda}\times\int_{-\infty}^{\Omega_F}d\Omega_0\int_{-\infty}^{\Omega_0}d\Omega(\Omega_0-\Omega)^{1/2}\mathrm{Re}\bar{G}^R(\Omega)\mathrm{Im}\bar{G}^R(\Omega)\,. \tag{2.11}$$

This equation together with Eqs. (2.9) and (2.10) is solved for λ in a self-consistent way.

The above theory has assumed that the carriers are scattered by the point charges of the ionized impurities. According to PS's results on localized states, the assumption may be justified for isocoric impurities but not for nonisocoric impurities. In the pseudoimpurity-theoretical discussion, PS have pointed out that if one insists on treating the bound states problem in terms of an "effective" mass for nonisocoric impurities, one can formally define a mass which is given as an operator made up of an effective potential and a spatial derivative. Based on this consideration, the assumption made here is as follows. First, the dependence of the conductivity on the impurity species arises from the same dependence of the density of states in the energy range $\omega\leq\omega_c$. The value of ω_c is such that for $\omega\leq\omega_c$ the density of states is substantially modified by the impurity scattering. The density-of-states mass in the range $\omega\leq\omega_c$ should be changed from m_D to m_D' by assuming the mass operator to be a constant m_D'. Second, defining the effective Bohr radius a_H (different from a_B) giving measured binding energy E_b in the hydrogenic picture, i.e., $E_b=e^2/(2\epsilon_0 a_H)$ we assume $m_D'\propto a_H^{-1}$ for the conduction band. Especially for isocoric impurities we take $m_D'=m_D$. On the other hand, we calculate m_D' directly from $m_D'=\hbar^2\epsilon_0/(a_H e^2)$ for the valence band. The reason for the different definitions of the relation of m_D' to a_H is as follows. In the case of the valence band, on the one hand, a_H reflects the effects of the effective-mass anisotropy, of the core effect, and of the $\mathbf{q}$ dependence of the host lattice screening. Usually the last effect is not so important so that m_D' may be just $\hbar^2\epsilon_0/(a_H e^2)$ as long as the mass operator is assumed constant. In the case of the conduction band, on the other hand, a_H reflects, in addition to the above effects, that of the multivalley interaction so that m_D' cannot be put simply equal to $\hbar^2\epsilon_0/(a_H e^2)$. However, the multivalley interaction is, roughly speaking, proportional to the impurity potential. This is the reason why we take $m_D'\propto a_H^{-1}$, i.e.,

$$m_D'=\frac{E_b(\text{nonisocore})}{E_b(\text{isocore})}m_D \tag{2.12}$$

for n-type materials. Naturally, Eq. (2.12) is useful also for single-valley semiconductors as a special case.

III. RESULTS AND DISCUSSION

The theory in the preceding section is applied to Ge:As, Ge:Sb, Ge:Ga, Si:P, and Si:As of which experimental data of the conductivity at 4.2 K are available. The values of m_C and m_D for the conduction band (CB)

TABLE I. Material parameters for Ge and Si.

Material	Band	m_C/m_0	m_D/m_0	ϵ_0	ν
Ge	CB	0.12	0.22	15.4	4
Ge	VB	0.31	0.36	15.4	1
Si	CB	0.26	0.33	11.4	6

TABLE II. Empirical values characterizing localized states of various dopants in Ge and Si.

Material	Dopant	Type	(E_b) (meV)	n_c (cm^{-3})	a_H (Å)	m_D'/m_0
Ge	As	Isocoric donor	12.7	3.1×10^{17}	37	0.22
	Sb	Nonisocoric donor	9.6	1.4×10^{17}	48	0.17
	Ga	Isocoric acceptor	10.8	2.0×10^{17}	43	0.19
Si	P	Isocoric donor	45.3	5.7×10^{18}	14	0.33
	As	Nonisocoric donor	53.3	9.5×10^{18}	12	0.39

are calculated from $(m_\parallel/m_0, m_\perp/m_0)=(1.58,0.082)$ for Ge (Ref. 12) and (0.97,0.19) for Si,[12] where m_0 is the electron mass *in vacuo*. On the valence band (VB) of Ge, m_C and m_D which are calculated[12] by taking into account the heavy-hole band and the light-hole band on the basis of the warped energy surfaces are used. The band parameters are shown in Table I. Experimental values of E_b (Refs. 13 and 14) and of the critical impurity concentrations[15,16] n_c for the metal-insulator transition are shown in Table II together with the values of m_D' and a_H calculated from the E_b's. These values are practically the same as those calculated from empirical values on n_c shown also in Table II; for the calculation we have used the Mott relation[17] $a_H n_c^{1/3}=0.25$. The agreement between the values of m_D' obtained from both calculations indicates the usefulness of m_D' as a parameter for the description of low-energy states.

In practical calculations we adopt $\omega_c=(e^2\lambda/\epsilon_0)\gamma$ and

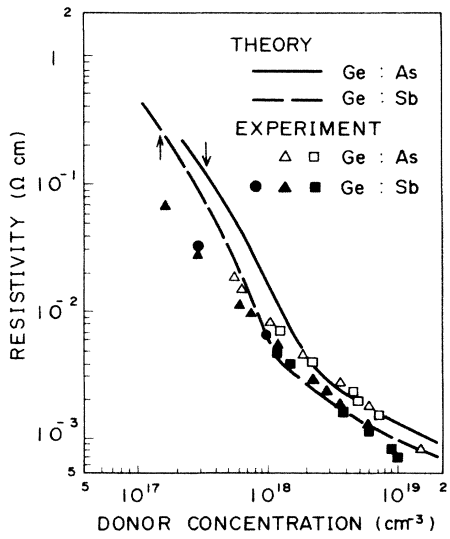

FIG. 1. Resistivities vs the donor concentration, which are obtained from the theory (solid and dashed lines) for 0 K and from experiments (open triangles, solid triangles, open rectangles, solid rectangles, and solid circles) at 4.2 K on Ge:As and Ge:Sb. Arrows show the empirical values of n_c.

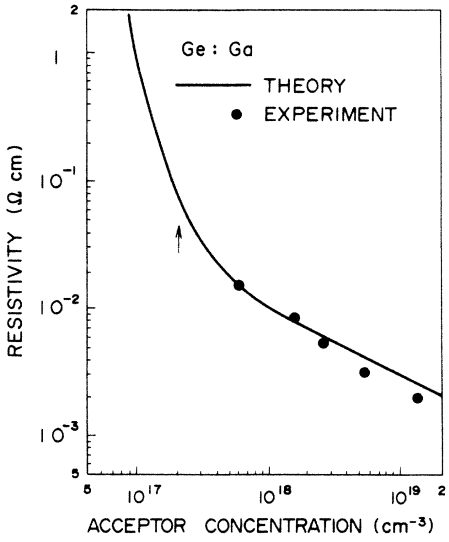

FIG. 2. Resistivities vs the acceptor concentration, which are obtained from the theory (solid line) for 0 K and from experiments (solid circles) at 4.2 K on Ge:Ga. An arrow shows the empirical value of n_c.

replace m_D in the equations of the previous section with $m_D'+(m_D-m_D')\exp[(\omega-\omega_c)/E_b]$ for $\omega\leq\omega_c$ in order to secure the continuous change of the density-of-states mass for convenience. It should be noted that $-\mathrm{Im}\bar{G}^R(\Omega)$ in Eq. (2.10) is different from zero only for $\Omega<\gamma$ and shows a peak at a value of Ω a little smaller than γ. This fact has aided us to find the effective range of ω where the density of states is substantially modified by the impurity scattering. Actually, the calculated values of the conductivity are found to be only weakly dependent on ω_c in a range $0\lesssim\omega_c\lesssim(e^2\lambda/\epsilon_0)\gamma$. Thus the choice of ω_c is not a critical problem.

Figures 1–3 show the conductivities as functions of

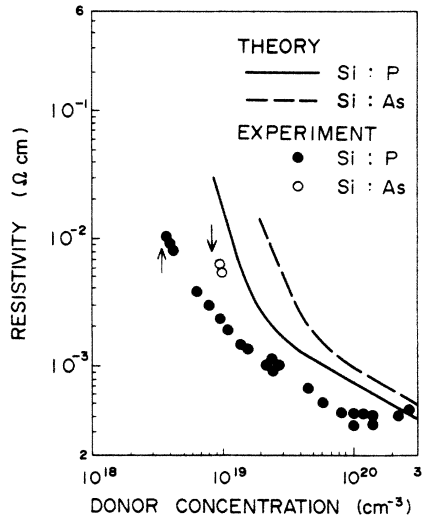

FIG. 3. Resistivities vs the donor concentration, which are obtained from the theory (solid and dashed lines) for 0 K and from experiments (solid and open circles) at 4.2 K on Si:P and Si:As. Arrows show the empirical values of n_c.

donor or acceptor concentration which are obtained from the present theory (lines) and experiments (points). In Fig. 1, the solid line, the open triangles,[18] and the open rectangles[8] are for Ge:As, and the dashed line, the solid triangles,[18] the solid rectangles,[8] and the solid circles[19] are for Ge:Sb. In Fig. 2 the solid line and the solid circles[19] are for Ge:Ga. In Fig. 3 the solid line and the solid circle[20] are for Si:P, and the dashed line and the open circles[16] are for Si:As. The experimental points are plotted only in the range $n > n_c$. The theoretical curves are shown only in the concentration range where the calculated σ_2 is negative. If the concentration is decreased to values below about n_c, σ_2 becomes positive. This implies that the bent-band model used in the theory is not a useful approximation below n_c as discussed previously.[10] Comparison between the present theory and the earlier ones for Ge:As is found in a previous paper.[10]

It is seen that the agreement between the theory and the experiments is excellent for Ge of both types except the range around n_c and is somewhat worse for Si. The As and P are isocoric donors in Si and Ge, respectively, and the Ga is an isocoric acceptor in Ge. On the other hand, the Sb and As are nonisocoric donors in Ge and Si, respectively. From this viewpoint it is seen that the theory well explains the dependence of the conductivity on the donor species in both Ge and Si. Unfortunately, we have no experimental data on nonisocoric acceptors, but the important point is that as seen in Fig. 2 the determination of m_D' directly from the measured value of E_b is quite useful for the acceptor which is very different from the hydrogenic picture: In fact, we have m_D' very different from m_D for Ge:Ga. However, the reason for the slight discrepancy between the theory and the experiments on Si is not clear. One possible reason might be that for a small value of a_H as in Si the bent-band model is not so powerful. A detailed study of this problem will be a future subject.

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[1]E. Conwell and V. L. Weisskopt, Phys. Rev. **69**, 258 (1946).
[2]H. Brooks, Adv. Electron. Electron Phys. **7**, 85 (1955).
[3]R. B. Dingle, Philos. Mag. **46**, 831 (1955).
[4]P. Csavinsky, Phys. Rev. **126**, 1436 (1962); **131**, 2033 (1963); **135**, AB3 (1964).
[5]Yu V. Gulyaev, Fiz. Tverd. Tela **1**, 422 (1959) [Sov. Phys.—Solid State **1**, 381 (1959)].
[6]D. Howarth and E. H. Sondheimer, Proc. Phys. Soc. London, Sect. A **219**, 53 (1953).
[7]H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).
[8]M. J. Katz, Phys. Rev. **140**, A1323 (1965).
[9]T. Kurosawa and W. Sasaki, J. Phys. Soc. Jpn. **31**, 953 (1971).
[10]M. Takeshima, Phys. Rev. B **36**, 1186 (1987).
[11]S. T. Pantelides and C. T. Sah, Phys. Rev. B **10**, 621 (1974); **10**, 638 (1974).
[12]E. H. Putley, *The Hall Effect and Related Phenomena* (Butterworths, London, 1960), pp. 101–106.
[13]T. H. Geballe and F. J. Morin, Phys. Rev. **95**, 1085 (1954).
[14]R. L. Aggarwal and A. K. Ramdas, Phys. Rev. **140**, A1246 (1965).
[15]M. N. Alexander and D. F. Holcomb, Rev. Mod. Phys. **40**, 815 (1968).
[16]P. F. Newman and D. F. Holcomb, Phys. Rev. B **28**, 638 (1983).
[17]N. F. Mott, Can. J. Phys. **34**, 1356 (1956).
[18]Y. Furukawa, J. Phys. Soc. Jpn. **17**, 630 (1962).
[19]H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).
[20]C. Yamanouchi, K. Mizuguchi, and W. Sasaki, J. Phys. Soc. Jpn. **22**, 859 (1967).