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Carrier scattering by neutral divalent impurities in semiconductors: Theory and experiment

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We have developed a theoretical model describing carrier scattering by divalent impurities in semiconductors. The mobility predicted by the model based on the scattering of electrons by helium atoms shows excellent agreement with the low-temperature mobilities measured for three Ge samples doped with different double acceptors; Be, Zn, and Hg. We show that the scattering cross sections of these double acceptors are the same despite the large difference in ionization energies. This supports our assumption that the contribution of the central-cell potential to neutral impurity scattering is negligible. [S0163-1829(97)06328-5]

I. INTRODUCTION

The development of the hydrogenic-effective-mass model for shallow impurities in semiconductors has led to the quantitative understanding of a wide variety of physical properties such as the far-infrared impurity absorption spectra[1] and the free-carrier mobility limited by neutral shallow-impurity scattering.[2] The model is based on the scaling of the atomic hydrogen in vacuum to a semiconductor by using the semiconductor material-dependent dielectric constant and the carrier effective mass. The success of the hydrogenic-effective-mass model has motivated researchers to develop the ''He-effective-mass model'' for divalent impurities by starting from the analysis of the atomic helium in vacuum. The resulting agreement between the He-effective-mass model and the double donor (acceptor) absorption spectra in Si and Ge is excellent.[3] While the ground-state energy of divalent impurities shows large chemical shifts due to the effect of the central-cell potential, the excited states are well described by the He-effective-mass model because the wave functions of the excited electrons (holes) are spatially delocalized. It is therefore of great scientific interest to examine the applicability of the He-effective-mass model to other physical phenomena in semiconductors. In this work we develop a theoretical model for carrier scattering by neutral divalent impurities in semiconductors.

Scattering by neutral impurities is one of the principal mechanisms limiting the low-temperature carrier mobility in lightly compensated semiconductors. So far all the models for this scattering process have assumed that the cross section of the neutral scattering center in a semiconductor can be described by the electron-scattering cross section of the free hydrogen atom properly scaled to semiconductor materials.[4–6] This approach has been successfully used by us to calculate low-temperature electron and hole mobilities in Ge doped with hydrogenic impurities.[2] However, attempts at applying the hydrogenic model to the scattering by neutral double donors[7] and acceptors[8] have met with very limited success. Understanding this scattering mechanism is of technological importance, for example, for the modeling of the performance of Ge:Be and Ge:Zn low-temperature photoconductors that are widely used by astronomers and astrophysicists.[9]

The theoretical model describing carrier scattering by neutral divalent impurities presented in this paper is based on the electron-scattering cross sections of a helium atom in vacuum. It should be applicable to a wide range of scattering problems involving double donors and acceptors in semiconductors. Strong support for our model will come from the direct comparison between theoretical and experimental low-temperature Hall mobilities for Ge:Be, Ge:Zn, and Ge:Hg samples.

II. THEORY

A. Neutral impurity scattering

Figure 1 shows the electron-scattering cross sections of hydrogen (H) and helium (He) in vacuum as a function of incident electron energy. Electrons with energy less than 10 eV are scattered more efficiently by H while those larger than 10 eV are scattered more by He. This feature, shown in Fig. 1, suggests that the mobilities predicted by the H- and He-based models will have different dependencies on temperature.

Meyer and Bartoli have shown that the electron-hydrogen (e^--H) scattering cross sections σ_H in vacuum can be approximated by[6]

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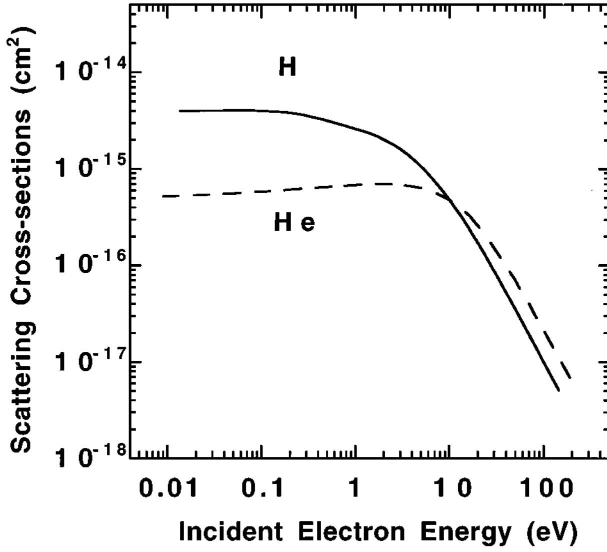

FIG. 1. Scattering cross sections of H and He in vacuum.

$$\sigma_{\mathrm{H}}(w)=A_{\mathrm{H}}(w)a_0/k, \quad (1)$$

with

$$A_{\mathrm{H}}(w)=\frac{35.2}{w^{1/2}}\frac{(1+e^{-50w})(1+80.6w+23.7w^2)}{(1+41.3w+133w^2)} \times\left[\frac{1}{w}\ln(1+w)-\frac{(1+0.5w-0.167w^2)}{(1+w)^3}\right], \quad (2)$$

where a_0 is the Bohr radius of the hydrogenic center and k is the magnitude of the wave vector of the incident electron. $w=E_{\mathrm{Inc}}/E_B$ is the scaled energy of the incident electron where E_{Inc} is the energy of an incident electron and E_B is the electron binding energy of the scattering center. From Eqs. (1) and (2) one can derive the scattering rate τ_{H}^{-1} for neutral hydrogenic impurity scattering:[6]

$$\tau_{\mathrm{H}}^{-1}=\frac{A_{\mathrm{H}}(w)\kappa N_N\hbar^3}{m_d^{*2}e^2}, \quad (3)$$

where κ is the dielectric constant, N_N is the neutral impurity concentration, and m_d^* is the density-of-states effective mass. The mobility calculation based on Eqs. (2) and (3) has been shown to agree very well with experimentally measured low-temperature Hall mobilities of Ge:As and Ge:Ga single crystals.[2]

The model based on electron-helium (e^--He) scattering proposed in this work is constructed in a similar manner. Figure 2 shows $A_{\mathrm{He}}(w)$ for e^--He scattering in vacuum calculated by Saha[10] and Nesbet[11] and determined experimentally by Register, Trajmar, and Srivastava.[12] The fitting of these results with an equation similar to Eq. (2) leads to a function $A_{\mathrm{He}}(w)$ in Eq. (1) for e^--He scattering (solid curve in Fig. 2):

$$A_{\mathrm{He}}(w)=\frac{6.1}{w^{1/2}}\frac{(1+e^{-35.7w})(1+64.1w+2.0w^2)}{(1+12.5w+8.6w^2)} \times\left[\frac{1}{w}\ln(1+w)-\frac{(1+0.5w-0.167w^2)}{(1+w)^3}\right]. \quad (4)$$

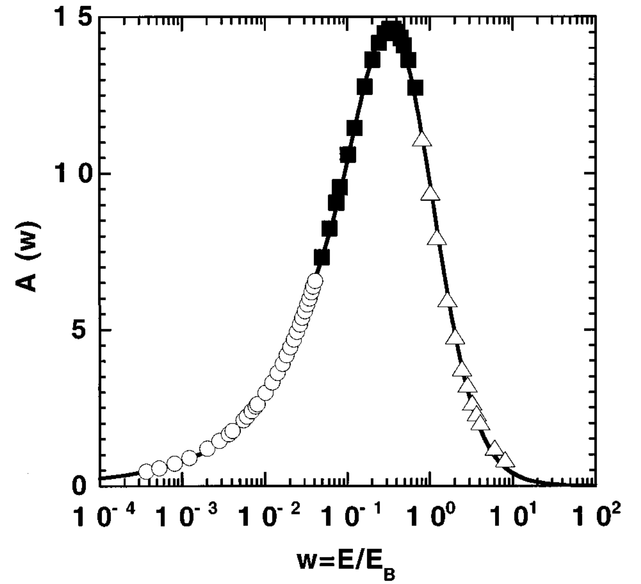

FIG. 2. $A(w)$ for e^--He scattering given by Saha (Ref. 10) (○), Nesbet (Ref. 11) (■), and Register, Trajmar, and Srivastava (Ref. 12) (△). The solid curve is the fit given by Eq. (4).

The rate τ_{He}^{-1} for neutral double donor/acceptor scattering is then given by

$$\tau_{\mathrm{He}}^{-1}=\frac{A_{\mathrm{He}}(w)\kappa N_N\hbar^3}{m_d^* m_{\mathrm{He}}^* e^2}, \quad (5)$$

where $m_{\mathrm{He}}^*=E_1 m_0\kappa^2/E_{\mathrm{He}}$ with $E_{\mathrm{He}}=24.6$ eV and E_1 is the ionization energy of the divalent scattering centers from their neutral to their singly ionized states. For the choice of E_1 it may seem appropriate to use the experimentally determined ionization energies which include contributions from central cores of impurities. However, we argue here that the appropriate choice of E_1 is the binding energy of the perfectly He-like impurity without a central-cell potential since scattering events are expected to take place far away from the impurity core where the potential is essentially Coulombic. For this case $m_{\mathrm{He}}^*=m_d^*$, i.e., Eq. (5) becomes

$$\tau_{\mathrm{He}}^{-1}=\frac{A_{\mathrm{He}}(w)\kappa N_N\hbar^3}{m_d^{*2}e^2}. \quad (6)$$

B. Total mobility calculation for doped Ge at low temperatures

In the following section we will compare directly the mobility calculation based on our neutral impurity scattering model with mobility measurements from p-type Ge:Be, Zn, and Hg samples. In this process the calculation requires the inclusion of not only neutral impurity scattering but also other important scattering mechanisms. Because neutral impurity scattering becomes dominant only at low temperatures ($T<40$ K), we include the contributions of three scattering mechanisms: neutral impurity, ionized impurity, and acoustic-phonon deformation-potential scattering. We ignore the contribution of optical-phonon deformation-potential scattering since it has a negligibly small effect at such low temperatures. In the following discussion we shall assume a

p-type semiconductor, i.e., $N_A > N_D$, where N_A and N_D are the acceptor and donor concentrations, respectively.

The neutral impurity scattering relaxation time $\tau_{\text{neutral}}^{-1}$ is calculated using our proposed model [Eqs. (4) and (6)]. Other models such as the hydrogenic model [Eqs. (2) and (3)] and the helium model with experimentally determined ionization energy [Eqs. (4) and (5)] are also used for comparison. The concentration of neutral impurity centers as a function of temperature $N_N(T)$ is given by

$$N_N(T) = N_A - N_D - p(T), \tag{7}$$

where $p(T)$ is the free hole concentration.

For the ionized impurity scattering, we employ the Brooks-Herring expression:[13,14]

$$\tau_{\text{ion}}^{-1} = \frac{\pi N_I e^4 (k_B T)^{-3/2} x^{-3/2}}{(2m_{\text{con}}^*)^{1/2}\kappa^2}\left[\ln\left(1+\frac{4x}{a}\right) - \frac{4x/a}{1+4x/a}\right]$$

$$\text{with } a = \frac{2\pi\hbar^2 e^2}{m^* \kappa k_B^2 T}\left(p + \frac{(N_A - N_D - p)(N_D + p)}{N_A}\right). \tag{8}$$

$x = E_{\text{Inc}}/k_B T$ (E_{Inc}: incident hole energy), $m_{\text{con}}^* = 0.28 m_0$ is the average conductivity effective mass for p-type Ge, and N_I is the ionized impurity concentration. The temperature dependent N_I is given by

$$N_I(T) = p(T) + 2N_D. \tag{9}$$

For the acoustic-phonon deformation-potential scattering,[15]

$$\tau_{\text{ac}}^{-1} = B_{\text{ac}} (m_{\text{con}}^* T)^{3/2} x^{1/2}, \tag{10}$$

where the constant $B_{\text{ac}} = 9.50 \times 10^8$ g$^{3/2}$ K$^{-3/2}$ for p-type Ge.[2]

Having found τ^{-1} of all three scattering mechanisms, we calculate an average $\langle \tau \rangle$ using the Maxwell-Boltzmann integration:

$$\langle \tau \rangle = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2} \exp(-x)}{\tau_{\text{ac}}^{-1} + \tau_{\text{ion}}^{-1} + \tau_{\text{neutral}}^{-1}}\, dx. \tag{11}$$

Finally the total Hall mobility μ_{total} is then given by

$$\mu_{\text{total}} = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} \frac{e \langle \tau \rangle}{m_{\text{con}}^*}, \tag{12}$$

where $\langle \tau^2 \rangle / \langle \tau \rangle^2$ is the Hall factor.

All the parameters except for the sample dependent N_A, N_D, and $p(T)$ are known. These three parameters will be determined precisely for each sample by performing variable-temperature Hall-effect measurements. Consequently all mobility calculations are performed without any adjustable or scaling parameters.

III. EXPERIMENTAL RESULTS AND DISCUSSION

We have measured the low-temperature Hall mobilities of Ge:Be and Ge:Zn samples. The Hall data of Ge:Hg taken with and without blackbody illumination given by Blakemore[8] are also used in our analysis. The melt-doped Ge:Be and Ge:Zn crystals used in this work were grown by the Czochralski method in H_2 atmosphere. Square-shaped samples ($8 \times 8 \times 0.8$ mm^3) were cut from each ingot and annealed at 700 °C for 3 h in N_2 atmosphere in order to dissociate all the acceptor-hydrogen complexes formed during the growth.[16] The van der Pauw contact configuration with boron implanted contacts at the four corners of each sample and a magnetic-field strength of 3000 G were employed in all Hall measurements.

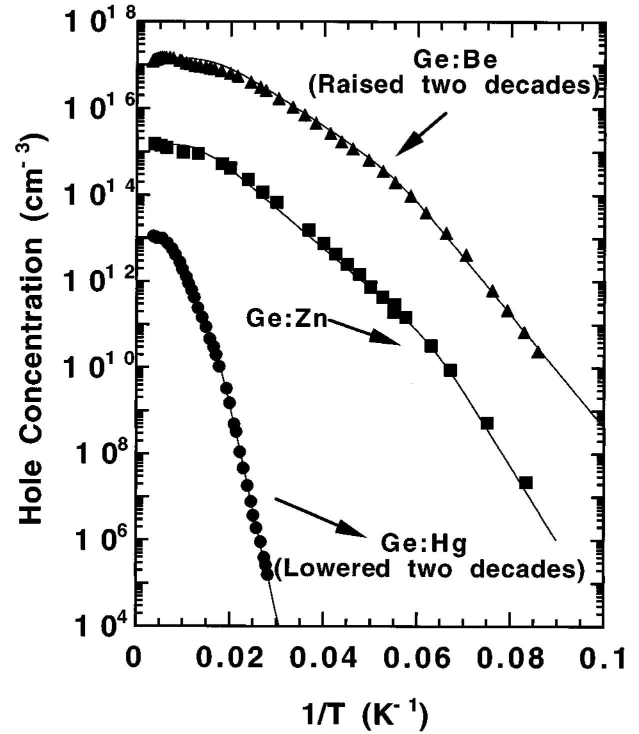

FIG. 3. Temperature-dependent hole concentration in Ge:Be (▲), Ge:Zn (■), and Ge:Hg (●). The solid curves are the best fits obtained with Eq. (13).

Be, Zn, and Hg in Ge are double acceptors and in their neutral state bind holes with ionization energies for neutral to singly ionized states (E_1) of 24.5, 33, and 91 meV, respectively. The binding energies for singly ionized to doubly ionized states (E_2) are 65, 87, and 230 meV for Be, Zn, and Hg, respectively. The relatively large variation of the binding energy E_1 arises from the different structures of the central-cell potentials. Without these central-cell potentials the binding energies of neutral Be, Zn, and Hg in Ge would be expected to be those of a perfectly He-like impurity ($E_B = 20.3$ meV), i.e., the scattering cross sections would be the same for all the impurities as described by Eq. (6). Figure 3 shows the temperature-dependent free hole concentration $p(T)$ of Ge:Be, Ge:Zn, and Ge:Hg samples taken in the dark. Since $E_1 \ll E_2$ for Be, Zn, and Hg, the experimentally determined $p(T)$ are fitted with standard freeze-out statistics for a semiconductor doped with monovalent acceptors containing only one ionization energy E_1:[17]

$$p + N_D = \frac{N_A}{1 + (gp/N_V)\exp(E_1/k_B T)}. \tag{13}$$

N_V is the effective density of valence-band states, $g = \frac{3}{2}$ is the spin degeneracy for double acceptors,[18] and E_1 is the ioniza-

TABLE I. N_A and N_D obtained from the Hall curve fittings.

Sample	N_A (cm^{-3})	N_D (cm^{-3})
Ge:Be	1.0×10^{15}	3.0×10^{12}
Ge:Zn	1.5×10^{15}	5.0×10^{10}
Ge:Hg	1.5×10^{15}	1.0×10^{12}

tion energy for neutral to singly ionized states. N_A and N_D obtained by fitting with Eq. (13) for each sample are shown in Table I.

Figure 4 shows the Hall mobilities in the three samples. The Ge:Hg data taken from Ref. 8 consist of the data measured in the dark (filled circles) and with the presence of illumination (open circles). The lines indicate three theoretical total Hall mobility calculations employing different neutral scattering models: (i) The He model [Eqs. (4) and (6)] with $E_1 = 20.3$ meV for a perfectly He-like acceptor (solid curves), (ii) the H model [Eqs. (2) and (3)] with $E_B = 11.2$ meV for a perfectly hydrogenic acceptor (broken curves), and (iii) the He model [Eqs. (4) and (5)] with the actual E_1 for each acceptor species, i.e., 24.5, 33, and 91 meV for Be, Zn, and Hg, respectively (dashed curves). Excellent agreement between calculation (i) and the experimental mobilities is demonstrated for all samples in strong support of our model based on e^--He scattering. It is also shown that the e^--H model, calculation (ii), underestimates the hole mobility and leads to an incorrect temperature dependence, while calculation (iii) with the central-core energy included overestimates the mobility indicating that the contribution of the central-cell potential to the scattering cross section is negligible.

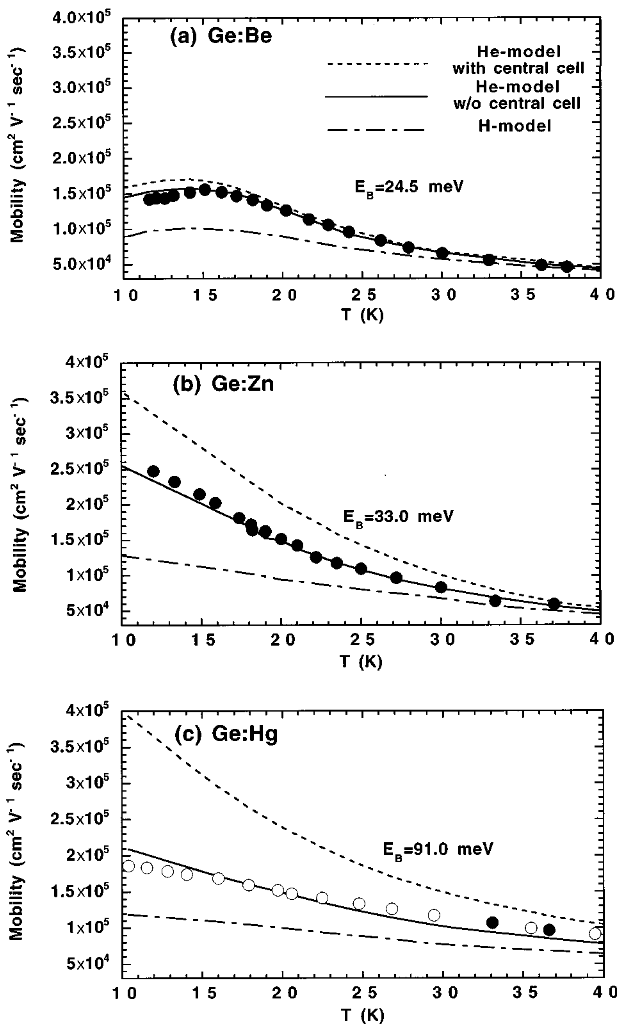

FIG. 4. Data points represent experimentally determined Hall mobilities in the dark (●) in (a) Ge:Be, (b) Ge:Zn, and (c) Ge:Hg samples. The Ge:Hg mobility data taken from Ref. 8 were measured with (○) and without (●) blackbody illumination. The solid, broken, and dashed curves are the result of calculations based on (i) our proposed model, the e^--He model without the central-cell contribution; (ii) the e^--H model, and (iii) the e^--He model with the central-cell contribution, respectively.

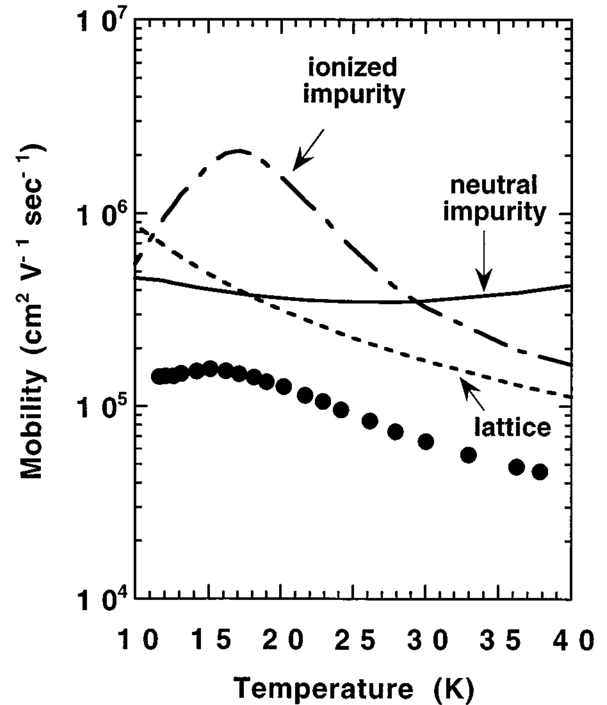

FIG. 5. The contributions of the different scattering mechanisms to the total mobility of the Ge:Be sample.

Finally, we show in Fig. 5 the contributions of different scattering mechanisms to the total mobility in Ge:Be. For the temperature range shown in Fig. 5, the relative contribution of neutral impurity scattering is much more significant than that of ionized impurity scattering due to the low doping compensation of the sample. The mobility due to acoustic-phonon deformation-potential scattering, on the other hand, is comparable with the one dominated by neutral impurity scattering. This is why it is important to include other scattering mechanisms especially acoustic-phonon deformation-potential scattering in our calculation. The appropriate computation of the mobility with no adjustable parameter allowed for the differentiation between various neutral impurity scattering models as shown in Fig. 4. It is also important to point out that the relative contribution of neutral impurity scattering is even larger in Ge:Zn and Ge:Hg than in Ge:Be throughout the temperature range of interest ($T = 10-40$ K) since the compensation ratios in Ge:Zn and Ge:Hg are much

smaller than that in Ge:Be. Also the hole concentrations $p(T)$ in Ge:Zn and Ge:Hg are significantly smaller than that in Ge:Be at $T=10-40$ K as seen in Fig. 3, i.e., Eq. (7) shows that the neutral scattering center concentration N_N is much larger in Ge:Zn and Ge:Hg than that in Ge:Be. We therefore conclude with high confidence that the e^--He model developed [Eqs. (4) and (6)] in this work is an appropriate approach for the treatment of carrier scattering by neutral divalent impurities.

IV. CONCLUSION

We have developed a theoretical model describing carrier scattering by neutral double donors and acceptors in semiconductors. An accurate and widely applicable analytical expression for the relaxation time has been obtained and used to calculate the Hall mobility limited by the scattering of holes by neutral double acceptors in Ge. Experimentally determined Hall mobilities agree very well with the values obtained from the model.

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