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THEORETICAL ANALYSIS OF THE EFFECT OF CARRIER DEGENERACY ON THE SCREENING LENGTH IN DEGENERATE TERNARY CHALCOPYRITE SEMICONDUCTORS

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An attempt is made to study theoretically the effect of carrier degeneracy on the Debye screening length of the carriers in ternary chalcopyrite semiconductors, taking degenerate n-$CdGeAs_2$ as an example. It is found on the basis of a newly derived electron energy spectrum which includes various types of anisotropies in the energy spectrum that the screening length decreases with increasing electron concentration as expected for degenerate semiconductors and tetragonal crystal field effectively reduces the same length. Besides, the corresponding well-known results for isotropic parabolic energy bands are also obtained from the expressions derived.

1. Introduction

It is well-known that the Debye screening length of the carriers in semiconductors is a very important basic parameter, characterizing the screening of the Coulomb field of the ionized impurity centers by the free carriers. Moreover, it affects many of the special characteristics of semiconductor devices, the carrier mobilities under different mechanisms of scattering and carrier plasmas in semi-

conductors. Besides, the screening length is a very good approximation to the accurate self-consistent screening in the presence of band tails[1]. It may be mentioned in this context that screening length is also connected with the Einstein relation for the diffusivity-mobility ratio[2,3] and its use in screened Coulomb potential to represent the effect of an impurity ion in a lattice has extensively been adopted to illustrate the interaction between two colliding carriers in Auger effects in semiconductors. Furthermore, the screening length has been shown[4,5] to be significantly modified by the conditions of carrier degeneracy and has also been investigated[6,12] for degenerate semiconductors under various physical conditions. Nevertheless, it appears from the literature that the effect of carrier degeneracy on the screening length in ternary chalcopyrite semiconductors having non-parabolic and non-standard energy bands has yet to be theoretically investigated. This will make our analysis a generalized one since from the results we can obtain the corresponding well-known expressions for the isotropic parabolic energy bands. Moreover, these semiconductors are being increasingly used as non-linear optical materials[13-15] and light emitting diodes[16]. Rowe and Shay[17] have demonstrated that the quasi-cubic model[18] can be used to explain the observed splitting and symmetry properties of the conduction and valence bands at the zone center of the ternary chalcopyrite semiconductors. The *s*-like conduction band is singly degenerate and *p*-type valence band is triply degenerate. The latter splits into three sub-bands because of spin-orbit and crystal-field interactions. The largest contribution to the crystal-field splitting of the valence band occurs from the non-cubic potential[19]. Incorporating the anisotropic crystal potential to the Hamiltonian and the special features of the ternary chalcopyrite semiconductors, Kildal[20-21] proposed an $E - \vec{k}$ dispersion relation for the conduction electrons in the same semiconductor with the assumptions of isotropic momentum-matrix element and the spin-orbit splitting parameter, respectively. The experimental data on the absorption constant[22], the effective masses[23] and the optical third order susceptibility[24] in ternary chalcopyrite semiconductors have provided strong evidence for the validity of the Kildal model[20] according to which the conduction band in the same semiconductor corresponds to a single ellipsoid of revolution at the zone center in $\vec{k}$-space with the energy dependent mass anisotropy. It would therefore be of much interest to investigate theoretically the effect of carrier degeneracy on the screening length in degenerate ternary chalcopyrite semiconductors by generalizing the above model. In what follows, we shall generalize the Kildal model by incorporating the anisotropies in the two above mentioned band-parameters. We shall then study theoretically the doping dependence of the screening length by deriving the appropriate expression for the electron statistics, taking degenerate *n*-$CdGeAs_2$ as an example.

2. *Theoretical background*

The screening length of the electrons in semiconductors can, in general, be expressed[11] as

$$\frac{1}{L_D^2} = \frac{e^2}{\varepsilon_s} \int_0^\infty \varrho_0(E) \left[-\frac{\partial f_0(E)}{\partial E} \right] \mathrm{d}E \tag{1}$$

where e is the electron charge, ε_s is the semiconductor permittivity, $\varrho_0(E)$ is the density-of-states function of the electrons, E is the electron energy as measured upward from the edge of the conduction band, $f_0(E)$ is the Fermi-Dirac occupation probability factor and is given by $f_0(E) = [1 + \exp((E - E_F)/k_B T)]^{-1}$ in which E_F is the Fermi energy as measured from the edge of the conduction band, k_B is the Boltzmann constant and T is the temperature. It appears, then, that the derivation of the screening length using equation (1), requires an expression of the density-of-states function which, in turn, is determined by the $E - \vec{k}$ dispersion relation of the conduction electrons. Incidentally, following Kildal[20], the form of the $\vec{k} \cdot \vec{p}$ matrix for ternary chalcopyrite semiconductors can be written as

$$H = \begin{bmatrix} H_1 & H_2 \\ H_2^+ & H_1 \end{bmatrix} \tag{2}$$

where

$$H_1 \equiv \begin{bmatrix} E_g & P_{\|} k_z & 0 & 0 \\ P_{\|} k_z & -\left(\delta + \frac{\Delta_{\|}}{3}\right) & \frac{\sqrt{2}}{3}\Delta_{\perp} & 0 \\ 0 & \frac{\Delta_{\perp}}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad H_2 \equiv \begin{bmatrix} 0 & 0 & x_{\cdot -} & x_{\cdot +} \\ 0 & 0 & 0 & 0 \\ -x_{\cdot -} & 0 & 0 & 0 \\ x_{\cdot +} & 0 & 0 & 0 \end{bmatrix},$$

E_g is the band gap, $P_{\|}$ is the momentum-matrix element along the c-axis, $\Delta_{\|}$ is spin-orbit splitting parameter along the c-axis, k_z is the longitudinal component of the wave-vector along the direction of c-axis, δ is the crystal-field splitting parameter, $\Delta_{\perp}$ is the spin-orbit splitting parameter in a plane perpendicular to the c-axis, $x_{\pm} \equiv [(P_{\perp}/\sqrt{2})(k_x \pm \mathrm{i}\, k_y)]$, $P_{\perp}$ is the momentum matrix element in a direction perpendicular to the c-axis and $\mathrm{i} \equiv \sqrt{-1}$.

Thus, neglecting the contribution of the higher bands and the free electron energy, the diagonalization of the above matrix leads to the generalized expression of the dispersion relation of the conduction electrons in bulk specimens of ternary chalcopyrite semiconductors as

$$\gamma(E) = f_1(E)\, k_s^2 + f_2(E)\, k_z^2 \tag{3}$$

where

$$\gamma(E) \equiv E(E + E_g)\left[(E + E_g)(E + E_g + \Delta_{\|}) + \delta\left(E + E_g + \frac{2}{3}\Delta_{\|}\right) + \frac{2}{9}(\Delta_{\|}^2 - \Delta_{\perp}^2)\right],$$

$$k_s \equiv [k_x^2 + k_y^2]^{1/2}$$

is the component of the transverse wave-vector in a plane perpendicular to the c-axis,

$$f_1(E) \equiv \left[2m_\perp^* \left(E_g + \frac{2}{3}\Delta_\perp\right)\right]^{-1} \hbar^2 E_g (E_g + \Delta_\perp)\left[(E + E_g)\left(E + E_g + \frac{2}{3}\Delta_{||}\right) + \right.$$

$$\left. + \delta\left(E + E_g + \frac{\Delta_{||}}{3}\right) + \frac{1}{9}(\Delta_{||}^2 - \Delta_\perp^2)\right],$$

$m_{||}^*$ is the transverse effective mass at the edge of the conduction band,

$$f_2(E) \equiv \hbar^2 E_g (E_g + \Delta_{||})\left[2m_{||}^*\left(E_g + \frac{2}{3}\Delta_{||}\right)\right]^{-1}\left[(E + E_g)\left(E + E_g + \frac{2}{3}\Delta_{||}\right)\right]$$

and $m_{||}^*$ is the longitudinal effective mass at the edge of the conduction band.

The use of Eq. (3) leads to the expression of the density-of-states function of the electrons as

$$\varrho_0(E) = (3\pi^2)^{-1}\varphi(E) \tag{4}$$

where

$$\varphi(E) \equiv \left[\frac{3}{2}\{\gamma(E)\}^{1/2} \cdot A(E)\{f_1(E) f_2(E)\}^{-1} - \{\gamma(E)\}^{3/2} B(E) \times\right.$$

$$\left. \times \{f_1(E)\}^{-2}\{f_2(E)\}^{-1/2} - \frac{1}{2}\{\gamma(E)\}^{3/2} C(E)\{f_1(E)\}^{-1}\{f_2(E)\}^{-3/2}\right],$$

$$A(E) \equiv [\gamma(E)\{(E)^{-1} + (E + E_g)^{-1}\}] + E(E + E_g)(2E + 2E_g + \delta + \Delta_{||}),$$

$$B(E) \equiv \left[2m_\perp^*\left(E_g + \frac{2}{3}\Delta_\perp\right)\right]^{-1} \hbar^2 E_g (E_g + \Delta_\perp)\left(2E + \delta + \frac{2}{3}\Delta_{||} + 2E_g\right)$$

and

$$C(E) \equiv \hbar^2 E_g (E_g + \Delta_{||})\left[2m_{||}^*\left(E_g + \frac{2}{3}\Delta_{||}\right)\right]^{-1}\left((2E + 2E_g + \frac{2}{3}\Delta_{||}\right).$$

Thus combining Eqs. (4) and (1) we get

$$L_D = [C_0\{\varphi(E_F) + \psi(E_F)\}]^{-1/2} \tag{5}$$

where

$$C_0 \equiv [e^2/3\pi^2\varepsilon_s],$$

$$\psi(E_F) \equiv \sum_{r=1}^{s} (k_B T)^{2r} \cdot \Theta_r \cdot \frac{\mathrm{d}^{2r}}{\mathrm{d}E_F^{2r}}[\varphi(E_F)],$$

$$\Theta_r \equiv 2\,[1 - 2^{1-2r}]\,\zeta(2r),$$

r is the set of real positive integers and $\zeta(2r)$ is the zeta function of order $2r$[25].

It appears then, that, the evaluation of screening length as a function of electron concentration requires a relation between the electron concentration and Fermi energy. Therefore, combining equation (4) with the Fermi-Dirac occupation probability factor, the electron statistics can be expressed as

$$n_0 = (3\pi^2)^{-1} [M(E_F) + N(E_F)] \tag{6}$$

where

$$M(E_F) \equiv [\{\gamma(E_F)\}^{3/2}/\{f_1(E_F)\sqrt{f_2(E_F)}\}]$$

$$N(E_F) \equiv \sum_{r=1}^{s} (k_B T)^{2r} \cdot \Theta_r \cdot \frac{d^{2r}}{dE_F^{2r}} [M(E_F)].$$

Incidentally, under the substitutions $\delta = 0$, $\Delta_{\parallel} = \Delta_{\perp} = \Delta$ (the isotropic spin-orbit splitting parameter) and $m_{11} = m_{\parallel}^* = m^*$ (the isotropic effective electron mass at the edge of the conduction band) equation (3) assumes the form

$$\frac{\hbar^2 k^2}{2m^*} = \omega(E), \quad \omega(E) \equiv \frac{\left(E_g + \frac{2}{3}\Delta\right) E(E + E_g)(E + E_g + \Delta)}{E_g(E_g + \Delta)\left(E + E_g + \frac{2}{3}\Delta\right)} \tag{7}$$

which is the standard dispersion relation of the conduction electrons of Kane-type semiconductors and is known as three-band Kane model[26]. It is thus expected that, under these substitutions, the results derived in this paper should reduce into simpler forms for isotropic Kane-type energy bands. Using the above mentioned substitutions, the general forms of the screening length and the electron statistics for three band Kane model will, respectively, be given by equations (5) and (6) where

$$C_0 \equiv e^2 g_0 (\varepsilon_s)^{-1},$$

$$g_0 \equiv (3\pi^2)^{-1} (2m^*/\hbar^2)^{3/2},$$

$$\varphi(E_F) \equiv \frac{3}{2} G(E_F) [\omega(E_F)]^{1/2},$$

$$G(E_F) \equiv \omega(E_F) \left[(E_F)^{-1} + (E_F + E_g)^{-1} + (E_F + E_g + \Delta)^{-1} - \right.$$

$$\left. - \left(E_F + E_g + \frac{2}{3}\Delta\right)^{-1}\right],$$

$$\psi(E_F) \equiv \sum_{r=1}^{s} (k_B T)^{2r} \cdot \Theta_r \cdot \frac{d^{2r}}{dE_F^{2r}} [\varphi(E_F)]$$

and

$$M(E_F) \equiv (3\pi^2) g_0 [\omega(E_F)]^{3/2}.$$

It may be noted that the above expressions are quite general for Kane type semiconductors and should be used as such where Δ is of the order of E_g (e. g. in InAs). However, for $\Delta \to \infty$, Eq. (7) gets simplified into the form

$$E(1 + a_0 E) = \frac{\hbar^2 k^2}{2m^*}, \quad a_0 \equiv \frac{1}{E_g} \tag{8}$$

and is well-known as two-band Kane model[27]. Thus under the condition $\Delta \to \infty$, the general forms of the screening length and the electron statistics according to two-band Kane model will, respectively, be given by Eqs. (5) and (6) where

$$\varphi(E_F) \equiv \frac{3}{2}(1 + 2a_0 E_F)\,[E_F(1 + a_0 E_F)]^{1/2},$$

$$\psi(E_F) \equiv \sum_{r=1}^{s} (k_B T)^{2r} \cdot \Theta_r \cdot \frac{\mathrm{d}^{2r}}{\mathrm{d}E_F^{2r}}\,[\varphi(E_F)],$$

$$M(E_F) \equiv 3\pi^2 g_0\,[E_F(1 + a_0 E_F)]^{3/2}.$$

Incidentally, under the assumption $aE_F \ll 1$, the expressions for the Debye length and the electron concentration for two-band Kane model get simplified to

$$L_D = \left[\left(\frac{e^2 N_c}{(\varepsilon_s k_B T)}\right)\left\{F_{-\frac{1}{2}}(\eta) + \frac{15 a_0 k_B T}{4} F_{\frac{1}{2}}(\eta)\right\}\right]^{-1/2} \tag{9}$$

and

$$n_0 = \left[N_c\left\{F_{\frac{1}{2}}(\eta) + \frac{15 a_0 k_B T}{4} F_{\frac{3}{2}}(\eta)\right\}\right] \tag{10}$$

where $N_c \equiv 2(2\pi m^* k_B T/h^2)^{3/2}$, $\eta \equiv E_F/k_B T$ and $F_j(\eta)$ stands for one-parameter Fermi-Dirac integarls of order j as defined by Blakemore[28]. Eqs. (9) and (10) have already been reported in the literature[6] for Kane-type non-parabolic energy bands where energy band structures are defined by two-band Kane model. Incidentally, it is also interesting to note that for $a_0 \to 0$, i. e. for parabolic energy bands, equations (9) and (10) get further simplified as

$$L_D = [(e^2 N_c/\varepsilon_s k_B T)\, F_{-\frac{1}{2}}(\eta)]^{-1/2} \tag{11}$$

and

$$n_0 = N_c F_{\frac{1}{2}}(\eta) \tag{12}$$

which are the standard well-known relations.

3. Results and discussion

For n-$CdGeAs_2$ using equation (6) and the parameters[21]: $\Delta_{||} = 0.34$ eV, $\Delta_{\perp} = 0.36$ eV, $\delta = -0.21$ eV, $E_g = 0.57$ eV, $m^*_{\perp} = 0.039\, m_0$, $m^*_{||} = 0.030\, m_0$ and $T = 4.2$ K, we have computed the Fermi energy as a function of electron concentration as shown in Fig. 1 in which the same dependence is also plotted by

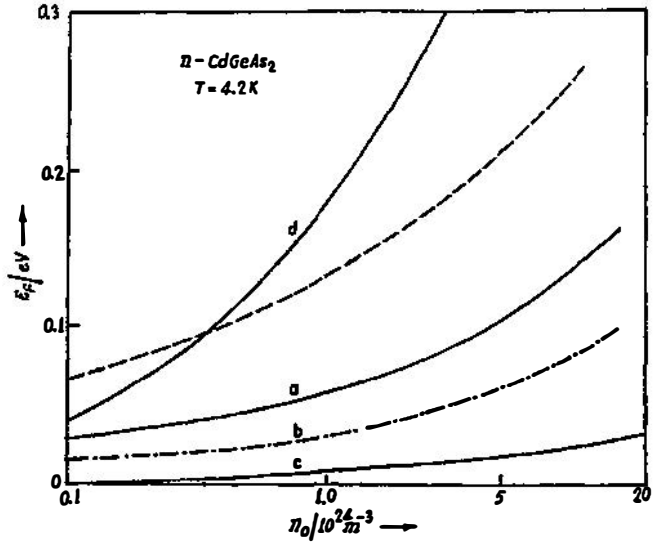

Fig. 1. Plot of the Fermi energy as a function of the electron concentration at 4.2 K in (a) degenerate n-$CdGeAs_2$, (b) degenerate three band Kane model with a band-edge effective mass $m^* = 0.02\, m_0$, (c) degenerate two band Kane model with the same effective electron mass and (d) degenerate parabolic band with the same effective mass. The dotted curve corresponds to $\delta = 0$.

taking the crystal-field parameter as zero for the purpose of comparison. In the same figure, the plots corresponding to degenerate 3-band Kane-model, degenerate 2-band Kane model and that for a degenerate parabolic band with an effective electron mass ($m^* = 0.02\, m_0$) which is of the order of mass[21] at the band edge of n-$CdGeAs_2$ are also shown. Using the appropriate equations together with the above parameters as used for obtaining Fig. 1 and taking $\varepsilon_s = 14.3\, \varepsilon_0$[21] we have further plotted the Debye screening length by using Eq. (5) as a function of the electron concentration in Fig. 2 in which the same dependence is also shown for $\delta = 0$ such that the effect of the crystal-field splitting on the same length could be immediately apparent. The simplified cases of a degenerate 3-band Kane model, degenerate 2-band Kane model and that of degenerate parabolic band have further been considered in Fig. 2.

It appears from Fig. 1 that the Fermi enegy increases with increasing carrier concentration at a rate lower than that corresponding to zero value of the crystal-field splitting parameter. Besides, the same parameter lowers the value of the Fermi energy in degenerate ternary chalcopyrite semiconductors as compared with that corresponding to $\delta = 0$ at a given value of the electron concentration

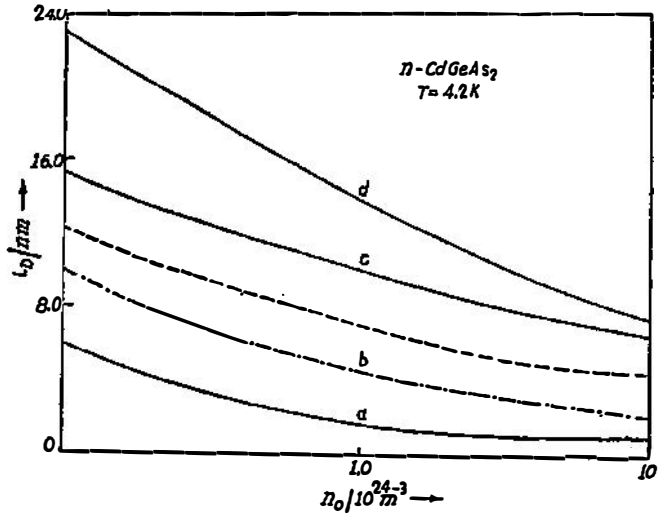

Fig. 2. Plot of the Debye screening length as a function of the electron concentration at 4.2 K in (a) degenerate n-$CdGeAs_2$, (b) degenerate three band Kane model with a band-edge effective mass $m^* = 0.02\ m_0$, (c) degenerate two band Kane model with the same effective electron mass and (d) degenerate parabolic band with the same effective mass. The dotted curve corresponds to $\delta = 0$.

in the whole range of the concentrations considered. For concentrations below $1 \times 10^{23}\ m^{-3}$, it is apparent from the same figure that the Fermi energies are in close agreement with each other. Though the Fermi energy also increases nonlinearly with concentration in the cases of degenerate 3-band Kane model, 2-band Kane model and also that of a degenerate parabolic band, the rates of increase are quite different from that in the proposed generalized band model. Fig. 2 shows that the screening length decreases with increasing electron concentration as expected for degenerate semiconductors. It is also seen that the crystal-field parameter affects the Debye screening length of the electrons quite significantly in degenerate ternary chalcopyrite semiconductors. For a fixed value of the electron concentration the screening length of the electrons is smaller as compared to that in the absence of crystalline field effects in the whole range of concentrations considered. It is observed that the dependence of the screening length on concentration is also determined by the band-shape because of its direct dependence on the Fermi energy. Besides, from the Fig. 2 we can also compare the screening length according to both the generalized dispersion relation and Kane-type band models since many authors have continuied to interpret the experimental data in terms of the isotropic Kane model for ternary chalcopyrite semiconductors. It is noted that the Kane model exhibits larger values of the screening as compared to those obtained from the proposed model. Besides, the differences between the screening lengths as determined from these two models can be seen to decrease with increasing carrier degeneracy. This suggests that the proposed model has to be strictly considered for relatively low values of the electron concentration so far as the screening effects are concerned. It is again noted that the effects of electron-electron interactions which become increasingly important with increasing electron concentration have not been considered in the present analysis. Besides, we have not considered the

formation of band-tails in degenerate semiconductors in the theoretical formulation of the screening length. These considerations would certainly improve the accuracy of the results. However, even in the absence of such modifications, the crystal-field splitting affects significantly the screening length of the electrons in degenerate ternary chalcopyrite semiconductors in the whole range of concentrations considered. Moreover, without consideration of many-body effects, the two models exhibit widely different screening lengths which become closer with increasing carrier degeneracy. It is, therefore, felt that the two models would still show widely different screening lengths in the presence of electron-electron interactions. Furthermore, it is apparent from Fig. 2 that the two models will give screening lengths in close agreement with each other only at very large values of the electron concentration due to reasons which are incidental and not due to electron-electron interaction effects. It is then likely that the results of the two models would not be in close agreement even at large electron concentrations if the electron-electron interaction effects are taken into consideration. Though the experimental verification of the basic content of this paper is not available to the best of our knowledge, this simplified analysis exhibits the major qualitative features of screening length in degenerate ternary chalcopyrite semiconductors under Thomas-Fermi approximation with reasonable accuracy. It may finally be noted that the basic aim of the present paper is not solely to investigate the screening length but also to formulate the electron statistics in ternary chalcopyrite semiconductors in its most generalized form since the various electron transport and the derivation of the expressions for many important physical parameters are based on the electron statistics in such materials.

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TEORIJSKA ANALIZA UTJECAJA DEGENERACIJE NOSILACA NABOJA NA DULJINU ZASJENJENJA U DEGENERIRANIM TERNARNIM HALKOPIRITSKIM POLUVODIČIMA

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Originalni znanstveni rad

Rad je pokušaj teorijskog proučavanja utjecaja degeneracije nosilaca naboja na Debyeevu duljinu zasjenjenja u ternarnim halkopiritskim poluvodičima, uzimajući za primjer degenerirani n-$CdGeAs_2$. Na osnovu novoizvedenog energetskog spektra koji uključuje razne vrste anizotropije nađeno je da duljina zasjenjenja prema očekivanju postaje manja kod veće koncentracije elektrona, i da tetragonalno kristalno polje efektivno smanjuje tu duljinu. Iz izvedenih izraza mogu se dobiti odgovarajući poznati rezultati za izotropne parabolične energetske vrpce.