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## IMPURITY STATES IN THE NARROW BAND-GAP SEMICONDUCTOR *n*-TYPE InSb

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We investigate impurity pair and triad formations in the narrow band-gap semiconductor *n*-doped InSb. It is found that in the region of the band-gap energy,  $E_g = 0.23$  eV, at 0 K, the effects of such clusters play a relevant role in the optical properties around and below the ionization energy of an isolated impurity (i.e.,  $E_i = 0.64$  meV). The transition for the uncompensated system is obtained as the concentration of impurities exceeds  $N_c = 4.7 \times 10^{13} \text{ cm}^{-3}$ . Copyright © 1996 Elsevier Science Ltd.

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THE INVESTIGATION of impurity states in the optical and transport properties of *n*-type InSb is a topic of continuous interest [1, 2]. This is mainly due to its importance in the fabrication of semiconductor devices, e.g. thin films [1], heterostructures, light-emitting and far-infrared laser devices [3], and quantum-dots [4, 5]. As such it is important to elucidate the controversy concerning the existence of an impurity band state separated from the conduction band [6–8]. Due to the very narrow band-gap of InSb,  $E_g = 0.23$  eV at 0 K [6], and the low ionization energy  $E_i = 0.64$  meV of the impurity atom we expect an influence of cluster states on the optical properties at very low temperature.

Recently, by measurements of magnetotransmission in the Faraday geometry, Choi *et al.* [8], have found evidence of a metallic impurity band around  $4 \times 10^{14} \text{ cm}^{-3}$ , above the observed impurity critical concentration for the metal–nonmetal (MNM) transition in compensated *n*-InSb, i.e.,  $N_c \approx 6.0 \times 10^{13} \text{ cm}^{-3}$  [6]. At lower donor concentrations

( $N_d \ll 10^{13} \text{ cm}^{-3}$ ) the infrared absorption spectra of individual donors are prominent. As  $N_d$  increases, donor pairs and donor triads appear, and the spectrum becomes nearly featureless, random clusters dominate the absorption. The data can be explained assuming a random distribution of donor sites. These pair and triad-impurity clusters were observed [9–11] by photoconductivity, absorption and resonant tunneling respectively, and analyzed in terms of random distribution of clusters [11–16].

As we know that such clusters are prominent below  $N_c$ , where the impurity band is expected to be present, we calculate the MNM transition. It is used as a random-like distribution of donors with the probability that the nearest neighbors lie at a distance  $R$ . We assume that the unperturbed impurity bandwidth  $\Delta\omega$  is given by the expression [17]

$$\Delta\omega = 2|\langle T \rangle|, \quad (1)$$

where  $\langle T \rangle$  is the average hopping integral. It is given by [17]

$$\langle T \rangle = \int T(R)P(R) dR, \quad (2)$$

where  $P(R)$  is the convoluted Poisson pair distribution

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function, given by

$$P(R) = \frac{3R^2}{R_d^2} \exp\left(\frac{-R^3}{R_d^3}\right), \quad (3)$$

where  $R_d = (4\pi N_d/3)^{-1/3}$ . The hopping between nearest sites is defined as

$$T = \int \Psi_i(r) H_1 \Psi_j(r-R) dr, \quad (4)$$

where  $H_i$  and  $\Psi_i$  are the one-particle Hamiltonian and wave function respectively. The transition is given by [17, 18]

$$\Delta w/U = 1.5, \quad (5)$$

where  $U$  is the intradonor Coulomb energy.

To determine the MNM transition we use the following parameters, effective mass  $m^* = 0.014m_0$  and effective Bohr radius  $a^* = 650 \text{ \AA}$  [6]. With these values we find the dielectric constant  $\epsilon = 17.2$  and the ionization energy of isolated impurity  $E_i = 0.64 \text{ meV}$ . The parameters used are more close to [5], [19] and [20] than those of [7] and [21]. Performing the calculation we find  $N_c$  for the uncompensated InSb to be  $N_c = 4.6 \times 10^{13} \text{ cm}^{-3}$ . The compensated  $N_c$  (compensation ratio  $K = N_a/N_d = 0.7$ , where  $N_a$  is the acceptor concentration) found by Ishida and Otsuka [6] was  $N_c \approx 6.0 \times 10^{13} \text{ cm}^{-3}$ . For this compensation, Thomanschesky and Holcomb [22] found for Si:P that  $N_c$  increased by 30% compared to the uncompensated system. For this percentage adding to our  $N_c$  we may conclude that it comes to the experimental finding.

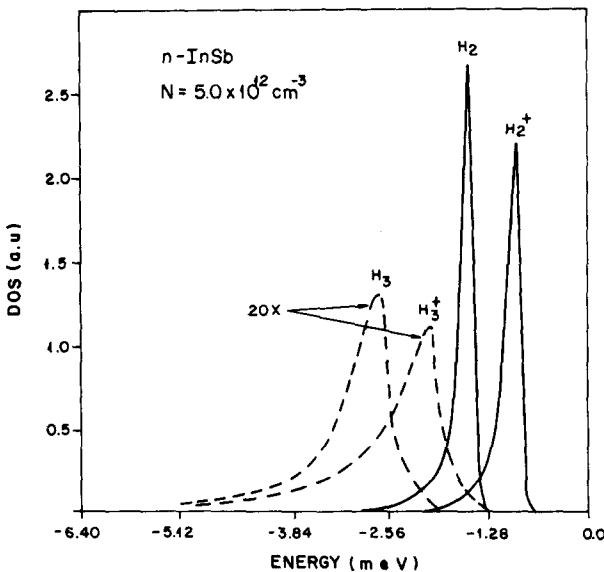


Fig. 1. Calculated density of impurity pair and triad states for *n*-InSb.

In the present work we also perform calculations to obtain the  $H_2$ ,  $H_2^+$ ,  $H_3$  and  $H_3^+$  densities of states and to verify that such clustering can be responsible for a bandwidth below the host conduction band and by extension, structures in the absorption spectra at lower energies. Disorder will cause a bandwidth in the density of states, which can be obtained as

$$D(E) = -\frac{1}{\pi} \text{Im} \langle \langle G^+(E, R) \rangle \rangle, \quad (6)$$

where  $\langle \langle \rangle \rangle$  means the average in disorder of the Green function propagator

$$\langle \langle G^+(E, R) \rangle \rangle = \left\langle \left\langle \sum_{\alpha} \frac{1}{E - E_{\alpha}(R) + i0^+} \right\rangle \right\rangle. \quad (7)$$

The contribution from the ground state of the four states (i.e.,  $H_2$ ,  $H_2^+$ ,  $H_3$  and  $H_3^+$ ) is then

$$\langle \langle G^+(E, R) \rangle \rangle^0 = \sum_{l=1}^4 \int P_n(R) [E - E_l^{\sigma}(R) + i\theta^+]^{-1} dR, \quad (8)$$

where  $P_n(R)$  is the pair for  $n = 2$  distribution function, given by equation (3), and the triad distribution function ( $n = 3$ ) as separation  $R$ . The last one is given by [16]

$$P_3(R) = 4\pi^2 N_d^2 C_c(R) \exp_3[-C'_3(R)N_d], \quad (9)$$

where

$$C_3(R) = \frac{4\pi}{3} \left[ R_0^3 + \frac{3}{4} R_0^2 R + \frac{R^3}{16} \right], \quad (10)$$

and

$$C'_3(R) = \frac{4\pi}{3} \left[ R_0^3 + \frac{3}{2} R_0^2 R + \frac{R^3}{8} \right], \quad (11)$$

where  $R_0 = 4a_0$  is the radius of the sphere centered at the donor. The distributions will enlarge the density of states with the donor concentration.

The ground state energy of  $H_2^+$  is very well known and the calculation for  $H_2$  is done within the framework of the alternant-molecular-orbital (AMO) approximation [13, 15, 23]. The calculation for the donor-triad molecules involve *ab initio* calculations of  $H_3$  and  $H_3^+$ . Within the Born-Oppenheimer approximation the total energies are calculated assuming a triangular form in  $D_{3h}$  symmetry. The Hartree-Fock self-consistent-field equations are solved expanding the atomic orbitals in a basis of Cartesian Gaussian-type functions [14, 16]. This basis is usually referred to as  $(9s3p1d/4s3p1d)$ . For more details about the calculations on  $H_2$ ,  $H_2^+$ ,  $H_3$  and  $H_3^+$  the reader should refer to [13-16] and [23].

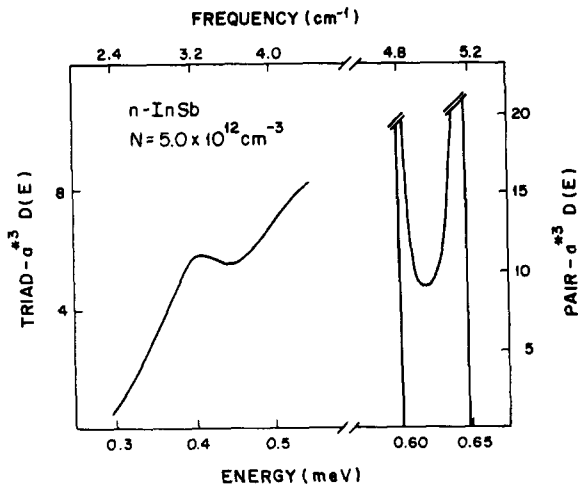


Fig. 2. Density of states associated to the infrared absorption due to the pair- and triad-donor molecules as a function of energy and frequency for *n*-InSb.

The results for the density of states at a low concentration of  $N = 5.0 \times 10^{12} \text{ cm}^{-3}$ , well below  $N_c$ , are shown in Fig. 1. Setting the zero at the bottom of the conduction band, we can see the impurity band formations due to the neutral and the ionized clusters of pair and triad molecules, respectively. They are responsible, for instance, for the tail at low energy below the ionization energy of an isolated impurity, i.e.  $E_i = 0.64 \text{ meV}$ . The impurity density of states associated with the absorption spectrum is obtained from Equation (6). It is given by

$$D(E) \approx \int P_n(R) \delta[E - E_1^0(R)] dR, \quad n = 2, 3, \quad (12)$$

where  $E_1^0(R) = E^0(H_n^+) - E^0(H_n)$  is the ionization energy of the lowest states of the pair-donor and triad-donor molecules. In Fig. 2 we show the results of *n*-InSb, as derived from equation (12), for an impurity concentration of  $N = 5.0 \times 10^{12} \text{ cm}^{-3}$ .

As we have seen in Fig. 1, the effects of donor-pairs are more apparent than those of donor-triads, causing accentuated peaks around the ionization energy of a single donor. These kind of structures were observed by Capizzi *et al.* [10]. The small peaks at lower energies are due to larger clusters. Here we identify a peak around  $0.4 \text{ meV}$ , and attribute it to the electron  $H_3 \rightarrow H_3^+$  transitions from their impurity ground states.

In conclusion, our results indicate that small clusters of impurities can influence the optical properties below the bottom of the conduction band at very low

concentration ( $N_d < N_c/10$ ) of the narrow-band gap semiconductor *n*-doped InSb.

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