EFFECT OF THREE-DONOR CLUSTER ON INFRARED ABSORPTION OF SEMICONDUCTOR SYSTEMS

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The density of states in n-doped Si in the intermediate impurity concentration range has been calculated for an interacting three-donor molecule. The results support the interpretation that the observed far infrared absorption at the energies below 30 meV is due to the electronic transition $H_3 \rightarrow H_3^+$ from their impurity ground states.

THE OPTICAL properties of interacting donor impurities in semiconductor systems have received a great deal of attention in solid state physics [1, 2]. From this point of view doped semi-conductors at a certain range of impurity concentration N have been extensively studied as an ideal case of optical absorptions by several investigators. The main effect upon increasing N on the optical absorption spectrum is to broaden the sharp atomiclike lines, which are well defined at very low N.

In our previous work [3] we have obtained two peaks at approximately $272\,\mathrm{cm}^{-1}$ and $286\,\mathrm{cm}^{-1}$ respectively, for $N \approx 10^{17}\,\mathrm{cm}^{-3}$, corresponding to the $H_2 \rightarrow H_2^+$ transition. This situation was for a random distribution of phosphorus in silicon (Si:P), with reasonable agreement to the absorption lines observed by Townsend [4] and Capizzi et al. [5]. Bajaj et al. [6] have speculated about the observed line "X" on the low energy side of the $1s$ to $2p$ transition. The position of this line is rather stringent, because it cannot be explained in terms of the transition between isolated impurities. A first attempt to explain such low energy, which is lower than that of the ionization energy of an isolated impurity center, was done by Nagasaka and Narita [7]. They have used the Heitler–London approximation for three-donor molecule scheme. Golka et al. [8–11] have also investigated the three-donor molecule for the ionization energy, electron affinity, metal-non-metal transition and far infrared absorption (FIA) in doped semiconductors. For FIA

they have used the ionization energy calculated from a version of the Hartree–Fock (HF) procedure for the semi-closed-shell system applied to H_3 and for H_3^+ at the HF approximation [8, 9].

Here we shall present a density of states (DOS) study of Si:P associated to the FIA, derived from the transition $H_3 \rightarrow H_3^+$. In our approximation this ionization energy of H_3 corresponds to the energy required to promote an electron from the three-donor-cluster (or three-impurity molecule) to the bottom of the conduction band.

All the calculations have been performed at the *ab initio* self-consistent-field (SCF) level utilizing the spin-Unrestricted Hartree–Fock (UHF) model. This assures proper dissociation into separate hydrogen atoms, for large interatomic distances, and gives a fair representation of the electronic energy. To solve the HF equations we expand the atomic orbitals in a basis of Cartesian Gaussian-type orbitals. The basis employed consists of $9s$ functions contracted to $4s$ and a set of three uncontracted p-type polarization functions, as suggested by Siegbahn and Liu [12]. This basis is usually referred to as $(9s\ 3p/4s\ 3p)$. Utilizing the Born–Oppenheimer separation the total electronic energy is solved for different interatomic distances.

We consider two configurations for the three-donor occupying the lattice sites, i.e., a linear symmetric configurations (L) and an equilateral triangle configurations (T). The total ground state energies of the systems H_3^+ and H_3, for both configurations, are shown in Fig. 1. For H_3, $R_{\mathrm{eq}}^l = 1.7\,a_0$ and $E_L(H_3) = -3.21$ Ry, $R_{\mathrm{eq}}^T = 1.89\,a_0$ and $E_T(H_3) = -3.03$ Ry, where R_{eq} is the equilibrium conformation. For H_3^+, $R_{\mathrm{eq}}^L = 1.51\,a_0$ and $E_L(H_3^+) = -2.45$ Ry, $R_{\mathrm{eq}}^T = 1.70$

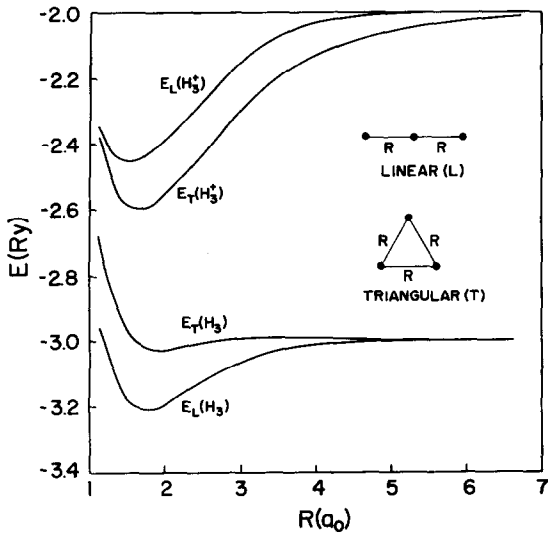* On leave from INPE/LAS, C.P. 615, 12210 São José dos Campos, SP, Brazil.

Fig. 1. Ground state energies of the H_3 donor molecule and H_3^+ donor molecular for linear (L) and triangular (T) configurations, as a function of the interatomic separation R. a_0 is the Bohr radius.

a_0 and $E_T(H_3^+) = -2.60$ Ry. The ionization energies as a function of R are shown in Fig. 2.

The triangular configuration requires less energy for ionization for all values of R. As it can be noted, for both configurations the energies are smaller than 1 Ry which is the ionization energy of a single donor. This aspect should influence the absorption spectra and transport properties.

The DOS associated to the FIA spectrum is given by

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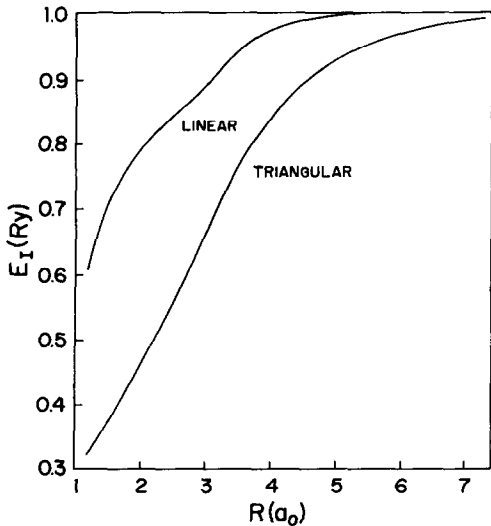

Fig. 2. Ionization energies of the three-donor molecule H_3 for different configurations, as a function of R.
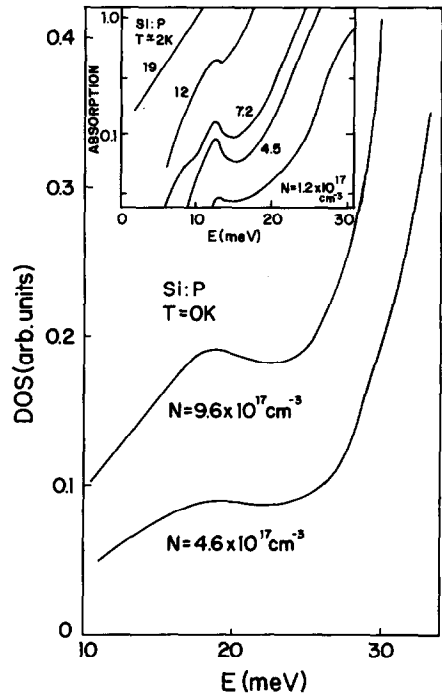

Fig. 3. Density of states associated to the far-infrared absorption due to the three-donor molecule as a function of energy. System Si:P. Inset shows the experimental data from Thomas et al. [2].

where $\langle\langle \ \rangle\rangle$ means an average disorder of the Green function propagator. For the ground state energy [3]

$$\langle\langle G^+(E, R)\rangle\rangle = \int P(R)[E - E_I(R) + i0^+]^{-1} dR \quad (2)$$

then

$$D(E) = \int P^\gamma(R)\delta(E - E_I^\gamma(R)) dR, \quad (\gamma = L \text{ or } T) \quad (3)$$

where $P(R)$ is the probability of the three-donor molecule at separation R. For the triangle configurations we have [7]

$$P^T(R) = 4\pi R^2 N^2 C_3(R) \exp[-C_3'(R)N] \quad (4)$$

with

$$C_3(R) = \tfrac{4}{3}\pi\left(R_0^3 - \tfrac{3}{4}R_0^2 R + \frac{R^3}{16}\right) \quad (5)$$

and

$$C_3'(R) = \tfrac{4}{3}\pi\left(R_0^3 + \tfrac{3}{2}R_0^2 R - \frac{R^3}{8}\right). \quad (6)$$

For the linear case we have [7]

$$P^L(R) = 4\pi R^2 N^2 C_3(R) \exp[-C_3''(R)N] \quad (7)$$

where

$$C_3''(R) = \tfrac{4}{3}\pi\left(R_0^3 + \tfrac{3}{4}R_0^2 R - \frac{R^3}{16} \right). \tag{8}$$

We have considered a sphere of radius $R_0 = 4a_0$ centered at the donor, based in the experiment of the N dependence of electron-spin-resonance [7, 13]. $E_i''(R) = E''(H_3^+) - E''(H_3)$, is the ionization energy of the ground state three-donor molecule.

In Fig. 3 we show the results for the DOS's, associated to the FIA spectra, as derived from equation (3) for different concentrations. These results are obtained for the triangular configurations. The linear case presents the same qualitative behaviour and therefore it is not shown. We have used the following atomic units for the systems Si:P. Effective Bohr radius $a_0^* = 17.3$ Å and dielectric constant $K = 11.7$. The absorption edge of the spectra is seen to move toward lower energies with increasing impurity concentration. The same behaviour is observed in the measurements of Thomas et al. [2] (inset in the Fig. 3) and Toyotomi [13]. For the controversial position of the line at $36\,\mathrm{cm}^{-1}$ of the n-GaAs, observed by Bajaj et al. [6], we found the value $36.8\,\mathrm{cm}^{-1}$ [14], which is in very good agreement.

Summarizing, our results support the interpretation that the observed FIA spectra, in the energy range considered in this paper, are due to the electronic $H_3 \rightarrow H_3^+$ transitions from their impurity ground states.

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