Impurity states in doubly doped systems: Investigation of donor-donor and donor-acceptor pairs

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In a recent paper, Yi and Neumark [Phys. Rev. B **48**, 17 043 (1993)] determined the effective radii of donors and acceptors in ZnSe:Na from the time decay of the close pairs. The pair decay rate used is proportional to an overlap integral between donor and acceptor wave functions. We show that such an integral as well as the hopping matrix can be used for both donor-acceptor and donor-donor systems. The density of states, calculated from these integrals, is capable of predicting the shift of conductivities observed in experimental results. The calculation for the metal-nonmetal transition of Si: P,B is in good agreement with recent experimental findings.

A number of measurements and calculations have attempted to describe, both quantitatively and qualitatively, the influence of the donor-acceptor and donor-donor pairs in the luminescence and metal-nonmetal (MNM) transition of semiconductor systems.[1-11] Recently Yi and Neumark[1] have determined the impurity radii of ZnSe:Na from the time decay of the donor-acceptor pairs. The pair decay rate used is proportional to an overlap integral between the wave functions of different donor and acceptor radii. It can be expressed in the form[1,4,5]

$$S(R) = f(\alpha, \beta, R) . \tag{1}$$

In deriving this equation, it was assumed that $\alpha = (1/a_D)$, where a_D is the donor radius, $\beta = (1/a_A)$, where a_A is the acceptor radius, and R being the separation between pairs. The overlap integral derived for shallow doubly doped systems is written as[9]

$$S(R) = \frac{8y^{5/2}}{(1-y^2)^2} \left\{ 1 + \frac{\exp(1-y)R^*}{y} + \frac{4[1-\exp(1-y)R^*]}{(1-y^2)R^*} \right\} \exp(-R^*) , \tag{2}$$

where $y = a_x/a_D$ and $R^* = R/a_x$. Here we identify a_x as acceptor or donor, i.e., $a_x = a_A$, $a_x = a_D$, or $a_x \neq a_D$ (a_x being a different kind of donor). With the substitutions of $y = \alpha/\beta$ and $R^* = \beta R$, Eq. (2) reduces to that given in Ref. 1 [i.e., Eq. (5) of Ref. 1]. The hopping matrix elements are obtained as

$$V(R) = \frac{4(\alpha\beta)^{3/2}}{(\alpha^2 - \beta^2)^2 R}$$
$$\times \{ 2\beta \exp(-\alpha R) + [(\alpha^2 - \beta^2)R - 2\beta]\exp(-\beta R) \} . \tag{3}$$

The above equations (2) and (3), were derived from the momentum transform, for the overlap $S(R)$ and

Coulomb hopping $V(R)$ integrals, respectively. For two functions $f_1(\mathbf{r})$ and $f_2(\mathbf{r} - \mathbf{R})$ we have the overlap

$$S(R) = \int d\mathbf{r} f_1(\mathbf{r}) f_2(\mathbf{r} - \mathbf{R}) . \tag{4}$$

It can be written in momentum space as

$$S(R) = \frac{1}{(2\pi)^3} \int d\mathbf{p} f_1(\mathbf{p}) f_2(\mathbf{p}) \exp(i\mathbf{p}\cdot\mathbf{R}) , \tag{5}$$

where

$$f_1(\mathbf{p}) = 8\sqrt{\pi}\alpha^{5/2} \frac{1}{(\alpha^2 + p^2)^2} \tag{6}$$

and

$$f_2(\mathbf{p}) = 8\sqrt{\pi}\beta^{5/2} \frac{1}{(\beta^2 + p^2)^2} . \tag{7}$$

For the hopping term, we have

$$V(R) = \int d\mathbf{r} g(\mathbf{r}) f_2(\mathbf{r} - \mathbf{R}) , \tag{8}$$

where

$$g(\mathbf{r}) = \frac{f_1(\mathbf{r})}{|\mathbf{r}|} . \tag{9}$$

Equation (8) can be expressed in terms of momentum space as

$$V(R) = \frac{1}{(2\pi)^3} \int d\mathbf{p} g(\mathbf{p}) f_2(\mathbf{p}) \exp(i\mathbf{p}\cdot\mathbf{R}) , \tag{10}$$

where

$$g(\mathbf{p}) = (\alpha^3/\pi)^{1/2} \frac{4\pi}{(\alpha^2 + p^2)} , \tag{11}$$

and $f_2(\mathbf{p})$ is given by Eq. (7).

We calculate the MNM transition by the Hubbard model when[7,8]

$$W/U = 1.15 , \tag{12}$$

where U, the correlation energy, is given by $U = 0.96E_B$ (E_B being the isolated binding energy),[7,8]
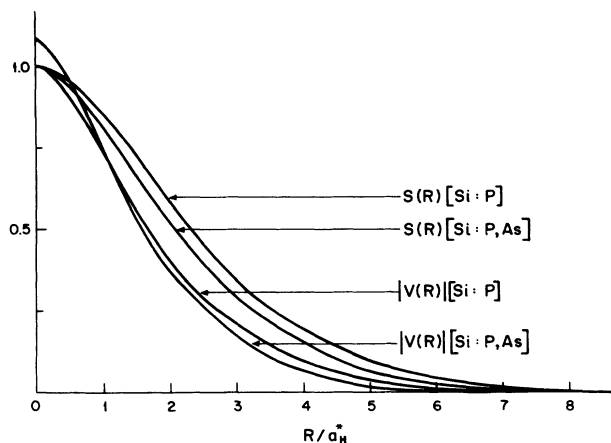
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FIG. 1. Overlap $S(R)$ and hopping $V(R)$ integrals as a function of R for Si:P and Si:P,As systems.

and W is the bandwidth and it is given by

$$W = 2Z|T(R)| , \qquad (13)$$

where Z is the coordination number for a particular arrangement of centers. Here, we carried out the calculations averaging three different structural arrangements of the centers (cubic, body-centered cubic, and diamond) to ensure that the results are not sensitive to a particular choice of Z (i.e., lattice). $T(R)$ is defined by[7,8]

$$T(R) = \int f^\alpha(\mathbf{r}) H f^\beta(\mathbf{r} - \mathbf{R}) d\mathbf{r} . \qquad (14)$$

In the above equation H is the Hamiltonian including the kinetic-energy operator and the electron-donor (-acceptor) interactions. It is written as

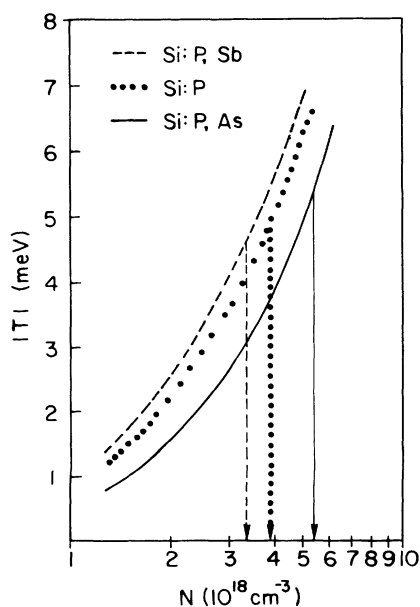$$T(R) = \frac{e^2}{Ka_D}\left[V(R) + \frac{S(R)}{2}\right] , \qquad (15)$$

FIG. 2. $T(R)$ as a function of N for different systems. The arrows indicate the impurity critical concentration for the MNM transition.
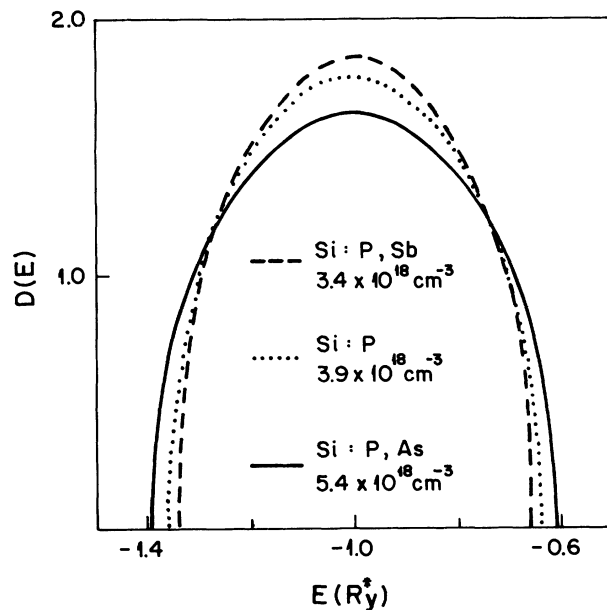

FIG. 3. Impurity density of states $D(E)$ as a function of effective Rydberg for different systems.

where K is the dielectric constant of the host material. Both U and $T(R)$ are scaled to the binding energy of Si:P, i.e., $E_B = 45.5$ meV.

In Fig. 1 we show the overlap and hopping integrals for Si:P,As and Si:P systems. In Fig. 2 we show $T(R)$ as a function of the impurity concentration N, for Si:P,As, Si:P, and Si:P,Sb. The arrows indicate the calculated critical concentration N_C for the MNM transition. The values of N_C obtained from Eq. (12) are $N_C(\text{Si:P,Sb}) = 3.4 \times 10^{18}$ cm^{-3}, $N_C(\text{Si:P}) = 3.9 \times 10^{18}$ cm^{-3}, and $N_C(\text{Si:P,As}) = 5.4 \times 10^{18}$ cm^{-3}. We assume that the concentrations of the two donors are equal.

To investigate any possible variation in the thermodynamic and transport properties, due to these doubly doped systems, we calculate their density of states. The density of states $D(E)$ is assumed to be parabolic and it is given by

$$D(E) = \{2[1 - (E/W)^2]^{1/2}/\pi W\} \quad \text{if } E \le W . \qquad (16)$$

The results for $D(E)$ are shown in Fig. 3 for the obtained N_C's which agree with experiments.[6,8] The effects of the doubly doped systems are reflected in the density of states, producing a different enhancement at the middle of the bands, where the Fermi energy is situated. This situation will cause, for the same impurity concentration, a shift in the specific heat and conductivity as well. In fact a shift was observed for the conductivity of Si:P,As compared to Si:P.[6]

With the scheme outlined above we have performed the calculation for the MNM transition of the donor-acceptor system Si:P,B. We found $N_C \approx 4 \times 10^{18}$ cm^{-3}. This value is consistent with recent experimental findings.[10,11]

Briefly, we have shown that the donor-acceptor pair scheme used for luminescence is equally used for doubly doped semiconductor systems.

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