SOME PROBLEMS OF HYBRIDIZATION AND OF THE DENSITY OF STATES SELF-CONSISTENT DETERMINATION IN SEMICONDUCTORS

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Abstract

A method which takes into account the hybridization of impurity (and conduction) band states is proposed, and an estimation of the importance of this effect is given (the change of the overlapp integral (Fig. 1)).

A complete procedure for self-consistent determination of the screening length λ, and the Fermi level is proposed, based on the fact that the perturbed density of states function depends on N and λ. The values of λ and η are the solutions of differential eq. (8b').

1. INTRODUCTION

A doped semiconductor is certainly the most experimentally studied disordered system. It provides a typical example of the metal-nonmetal (insulator) (m — i) transition at the critical (donor) concentration N_c ($\cong 3.8 \cdot 10^{18}$ cm^{-3} in S_i : P). However, it is known[1, 2, 3] that localized electrons exist on the metallic side of the m — i transitions, and the opposite is true for the insulating samples (nonlocalized electrons exist).

In this paper we shall analyse two points: (i) the importance of hybridization of impurity (and conduction) band states, and (ii) the complete self-cons. calculation of the screening length λ, taking into account that not only the distribution function (e. g.[4, 5] $f = (1 + \exp |(E - E_F)/kT|)^{-1}$), but also the density of states function ρ depends on the Fermi level E_F : $\rho = \rho\,|E, N(E_F)|$.

2. HYBRIDIZATION OF IMPURITY (AND CONDUCTION) BAND STATES

Since the analysis of metal-insulator transition of the impurity band within only the free-electron or the tight binding approximations is not entirely adequate, we shall use a model that includes both free and bound states, as well as their hybridization.

We start with the Hamiltonian in the form (electron-electron interaction neglected)

$$\hat{H} = E_d \sum_i C_i^{+} C_i + \sum_{i \neq j} t_{ij} C_i^{+} C_j + \sum_{\vec{k}} \epsilon_{\vec{k}}\, a_{\vec{k}}^{+}\, a_{\vec{k}} + \sum_{\vec{k}_1 \neq \vec{k}_2} V_{\vec{k}_1 \vec{k}_2}\, a_{\vec{k}_1}^{+}\, a_{\vec{k}_2} +$$

$$+ \sum_{i, \vec{k}} (V_{i\vec{k}}\, C_i^{+}\, a_{\vec{k}} + V_{i\vec{k}}^{*}\, a_{\vec{k}}^{+}\, C_i), \tag{1}$$

where

$$t_{ij} = \langle i | V_i | j \rangle, \; V_{\vec{k}_1 \vec{k}_2} = \sum_i \langle \vec{k} | V_i | \vec{k} \rangle, \; \epsilon_{\vec{k}} = \langle \vec{k} | T | \vec{k} \rangle,$$

$$V_{i\vec{k}} = \langle i | T | \vec{k} \rangle + \sum_j \langle i | V_j | \vec{k} \rangle \tag{2}$$

and where $| i \rangle$ represents the localized states electron wave function at the i-th impurity atom and $| \vec{k} \rangle$ is the Bloch function. With Green function in the form

$$G_{ca} \equiv \langle\langle C_i; a_{\vec{l}}^{+} \rangle\rangle_z = \langle\langle C_i; \vec{l} \rangle\rangle_z \equiv G_{i\vec{l}}, \; z = E + i\delta \tag{3}$$

the system of four coupled equations with G_{ij}, $G_{\vec{k}j}$, $G_{\vec{k}\vec{l}}$ and $G_{i\vec{l}}$ may be obtained. To find an approximate solution of this system is a difficult problem even if there was no hybridization ($V_{i\vec{k}} = 0$).

To solve this problem we start with $V_{\vec{k}\vec{l}} = 0$, i.e. with unperturbed conduction band, where our system reduces to 3 equations, with two of them containing the effective overlapp integral

$$t_{il}^{eff} = t_{il} + S_{il}, S_{il}(E) = \sum_{\vec{k}} \frac{V_{i\vec{k}} V_{l\vec{k}}^{*}}{z - \epsilon_{\vec{k}}} \tag{4}$$

and the third is without t_{il}^{eff}

$$G_{\vec{k}\vec{l}} = \left\{ \delta_{\vec{k}\vec{l}} + \sum_i V_{i\vec{k}}^{*}\, G_{i\vec{l}} \right\} / (z - \epsilon_{\vec{k}}). \tag{5}$$

Finally, it is possible to solve for $G_{\vec{k}\vec{l}}$ directly from (5), and for the other two equations approximate tight-binding solutions exist[6], so these 3 values may be used as the starting values for iterative solution of 4 „exact" coupled equations ($V_{\vec{k}\vec{l}} \neq 0$); these calculations are in progress.

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*) As a matter of fact, physically E_F, or η is a function of N.

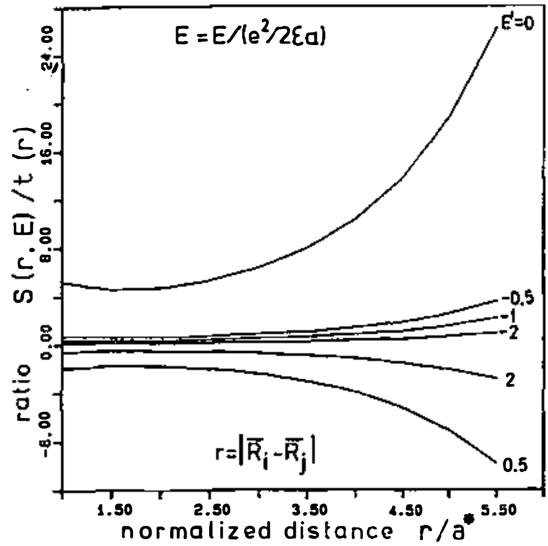

Fig. 1. – The ratio S(r, E)/t(r) for Si : P vs. r/a* with $E' = E/(I^2/2\epsilon a^*)$.

In order to estimate the importance of hybridization, we shall determine the difference $S_{ij} = t^{eff}_{ij} - t_{ij}$ using (4) and (2), which, with $|i>$ taken as the first Bohr orbital (effective radius a^*) and $|\vec{k}>$ as a plane wave, with

$$\sum_{\vec{k}} \to \frac{\Omega}{8\pi^3} \int d^3k \text{ and } r = |\vec{R}_i - \vec{R}_j|,$$

may be written in the form (the conduction band is taken to be parabolic with effective mass m^*, and the impurity potential to be purely Coulombic):

$$S(r, E) = \frac{8}{\pi a^{*3} r} \int_0^\infty \frac{h^2}{m^* a^*} \frac{k^2}{|k^2 + (a^*)^{-2}|^2} - \frac{e^2}{\epsilon} \frac{1}{k^2 + (a^*)^{-2}} \frac{k \sin kr\, dk}{E - \frac{h^2 k^2}{2m^*}} \tag{6}$$

3. THE COMPLETE SELF-CONSISTENT EVALUATION OF λ (N)

The neutrality equation (in heavily-doped semiconductor $p + p_a \ll n + n_d$ and $N_d \equiv N \gg N_a$) is given by

$$n + n_d = N = \int f \rho dE = \int_{-\infty}^{E_1(N)} f\rho_a dE + \int_{E_1(N)}^{\infty} f\rho_c dE \cong n = F(N, \lambda, \eta) \tag{7}$$

Having in mind that perturbed ρ – s depend explicitely on N and standard or effective standard deviations, σ (N, λ) or σ_{eff} (N, λ) (in parabolic unperturbed bands we have $\rho \sim \sqrt{E - E_{co}} \neq F(N, \lambda)$) and, as a consequence on N and λ which are implicite functions of the Fermi level*) or η, it is erroneous to put $\partial\rho/\partial\eta = 0$, as it was done in all previous works concerning this problem.

In (7) subscripts d and c denote donor and conduction band states, and $E_1(N)$ is the intercept energy (for the envelope density function max (ρ_d, ρ_c)), i.e. when $\rho_c = \rho_d$. In (7) we assume $N \cong n$ — all electrons non-localized. On the other hand, from the deffinition of the screening length λ, from (7) we obtain:

$$\frac{\epsilon}{e^2\lambda^2} \equiv \frac{\partial n}{\partial \eta} \cong \frac{\partial N}{\partial \eta} \doteq \int \frac{\partial f}{\partial \eta}\,\rho dE + \int f \frac{\partial \rho}{\partial \eta}\, dE, \qquad \eta = \frac{E_F}{kT} \qquad (8)$$

Thus, we have two cases:

a) $\partial\rho/\partial\eta = 0$ in (8), with $\partial f/\partial\eta = f\,(1-f)$, gives

$$\frac{\partial N}{\partial \eta} = \frac{\epsilon}{e^2\lambda^2} = \int f\,(1-f)\,\rho dE = F_a\,(N, \lambda, \eta), \qquad \text{and} \qquad (8a)$$

b) $\partial\rho/\partial\eta \neq 0$, implying that

$$\frac{\partial N}{\partial \eta} = \frac{\partial \rho\,(E; N, \lambda, \eta)}{\partial \eta} = \frac{\partial N}{\partial \eta}\,\phi_1\,(E; N, \lambda, \eta) + \frac{\partial \lambda}{\partial \eta}\,\phi_2\,(E; N, \lambda, \eta) +$$

$$+\ \phi_3\,(E; N, \lambda, \eta)$$

and (8) with $\partial N/\partial\eta = \epsilon/e^2\lambda^2$ may be written as

$$\frac{\partial N}{\partial \eta} = \frac{\epsilon}{e^2\lambda^2} = F_a\,(N, \lambda, \eta) + F_{13}\,(N, \lambda, \eta) + \frac{d\lambda}{d\eta}\,F_2\,(N, \lambda, \eta)$$

and finally we arrive to the differential equation

$$\frac{d\lambda}{d\eta} = F_b\,(N, \lambda, \eta) \qquad (8b)$$

In order to avoid the always uncertain numerical differentiation of eq. (7), according to (8), it should be better to perform this differentiation analytically, having some models for ρ_c and ρ_d (see e.g.[4, 7])):

$$\rho_d\,(E; N, \lambda) = \sqrt{\frac{2}{\pi}}\,\frac{N}{\sigma_{eff}}\,\exp\left\{-\left(\frac{E-E_d}{\sqrt{2}\,\sigma_{eff}}\right)^2\right\};\ \rho_c\,(E; N, \lambda) = \begin{cases} X + A_1\sqrt{\sigma}, & X < 0.6 \\ \sqrt{X\sigma}\,(1 - A_2/X^3), & X > 0.6 \end{cases} \qquad (9a, b)$$

where $X = (E - E_{co})/\sigma\sqrt{2}$. In both cases the second relation (for eq. 8a or 8b) is the eq. (7): $N = F(N, \lambda, \eta)$.

In case (a), $\partial\rho/\partial\eta = 0$ (representing an incomplete procedure) eqs. (7) and (8a) should be solved self-consistently:

– for N = const., assuming a value $\eta = \eta_1$, the value of λ_1 that gives the same N (to a specified accuracy) is calculated from (7);

– with $\lambda = \lambda_1$ in (8a) one gets the new $\eta = \eta_2$, and the process is repeated, as depicted in Fig. 2. Such a procedure was done for Si : P and the dependences λ (N) and $E_F - E_{co} = W_F$ (N) are given in Fig. 1 in7).

In case (b), the analytical differentiation gives (8b) and, provided the screening length is $\lambda = (\epsilon/e^2)^{1/2} (dN/d\eta)^{-1/2}$, we finally get

$$\frac{d^2N}{d\eta^2} = -2\left(\frac{e^2}{\epsilon}\right)^{1/2}\left(\frac{dN}{d\eta}\right)^{3/2} F_b\left(N, \frac{1}{\sqrt{dN/d\eta}}, \eta\right) = F_{b'}\left(N, \frac{dN}{d\eta}, \eta\right), \tag{8b'}$$

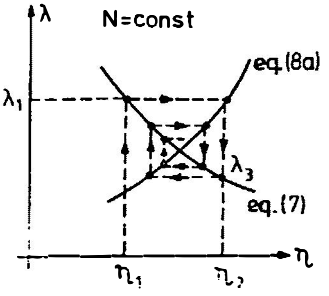

Fig.2 - Self-consistent procedure for the case (a): $\partial\rho/\partial\eta = 0$.

which can easily be solved (e.g. by Runge-Kutta method) as a second order differential equation, with initial conditions being the nondegenerate case solutions ($N_o \ll N_c$)

$$\lambda_o = \frac{\sqrt{\epsilon}}{e}\sqrt{\frac{kT}{N_o}}, \text{ and } N_o = B_c \exp\eta. \tag{10}$$

4. CONCLUSION

Considering a heavily-doped (n-type) semiconductor as a disordered system, we propose a model that includes the effect of hybridization. In this case, a system of 4 equations with 4 Green's functions is obtained, which reduces to the system of 3 equations for unperturbed conduction band, its solutions being the starting values for iterative solution of the „exact" problem (4 eqs.).

In order to estimate the influence of hybridization, the change, S_{il} or S(E,r), of the overlapp integral (4) is calculated from (6). As one can see from Fig. 1, this influence is greatest at the bottom of the intrinsic conduction band ($E = E_{co}$, $E' = 0$). This effect decreases with increase of $|E'|$, and it is still considerable for $E = E_d$ ($E' = -1$). Having in mind that ρ is determined by the value of S, considerable changes of both ρ_d and ρ_c can be expected.

In the second part of the paper it is pointed out that the perturbed density of states functions, ρ_d and ρ_c, depend on impurity concentration N, and screening length λ, implying that ρ's depend on the Fermi level E_F or $(E_F - E_{co})/kT = \eta$. A consequence of this is that the case $\partial\rho/\partial\eta = 0$, having been considered throughout the literature leads to an incomplete procedure for the self-consistent determination of λ and η. The proposed complete procedure (for $\partial\rho/\partial\eta \neq 0$) consists in solving the second order differential equation (8b'), with the initial conditions (10).

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