Theoretical electronic properties of silicon-containing bismuth

A. Ferreira da Silva[a)]
Instituto Nacional de Pesquisas Espaciais/INPE, Laboratorio Associado de Sensores e Materias, C.P. 515, 12201-970 São José dos Campos, SP, Brazil[b)]

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The electrical conductivities of n-doped silicon and, in particular Si:Bi, have been investigated for doping levels greater than the impurity critical concentration N_c for the metal-nonmetal transitions. A general feature of the conductivity for concentration normalized to N_c is presented in the order $\sigma(\mathrm{Bi})>\sigma(\mathrm{As})>\sigma(\mathrm{P})>\sigma(\mathrm{Sb})$. For Si:Bi, the value of N_c is calculated for different criteria. The mobility of electrons presents a lower value compared to Si:P. The results for Si:P and Si:As are compared to the experimental data available in the literature.

I. INTRODUCTION

Much attention has been given both theoretically and experimentally to the electronic properties of n-doped silicon for a long period, mainly for the Si:As, Si:P, and Si:Sb systems.[1–14] Bismuth-doped silicon (Si:Bi) was not given much attention. Maybe the reason is because Bi in Si has its ionization energy [$E_I(\mathrm{Bi})\approx 71$ meV], much larger than that of the other group-V elements, which have $E_I(\mathrm{As})\approx 53$ meV, $E_I(\mathrm{P})\approx 45$ meV and $E_I(\mathrm{Sb})\approx 42$ meV, respectively.[15–20] With such ionization energy the theory of the effective mass is expected to be less applicable to this impurity center.[15] Probably this is why the results on Bi were not worked out together with those of the other three donors, i.e., As, P, and Sb, respectively. However, the theory of the effective mass is used, with success, in the determination of E_I of chalcogen systems (group-VI elements) as Si:S, Si:Se, and Si:Te, which have $E_I \geqslant 100$ meV.[21,22]

Bismuth as a dopant in silicon has been investigated by ion implantation. It is a powerful method of making semiconductor devices.[23–25] This method also provides an ideal prototype to study disordered systems.[1,23]

Bearing in mind the importance of this system, we report here the calculations of some of its electronic properties, as metal-nonmetal (MNM) transition, electrical conductivity, and mobility as a first attempt to get to know its physical characteristics.

In 1973 and 1974 Berggren calculated the MNM transition for Si:Bi using two different ways, namely the Hubbard approach and Herzfeld theory, respectively.[17,18] Here we present four criteria to determine the MNM transition and a scheme to calculate the electric conductivity and, as a consequence, the mobility of conduction electrons.

II. MNM TRANSITION

For the MNM transition we have applied the following methods.

(i) The first is with use of the variation of the effective wave function and the interference factor due to the minima of the silicon conduction band. Disorder is neglected, and it is assumed that the unperturbed impurity bandwidth ΔW, is given by the expression[17,20,26–28]

$$\Delta W = 2Z|T|, \tag{1}$$

where Z is the coordination number for a particular arrangement of donors and T is the hopping energy between nearest neighbors. It is defined as

$$T = \int \psi_i(\mathbf{r}) H_1 \psi_j(\mathbf{r}) d\mathbf{r}, \tag{2}$$

where H_1 is the the one-particle Hamiltonian including the kinetic energy operator and the electron-donor interaction and ψ_1 is the wave function with the interference factor. The transition is given by[17,26,29,30]

$$\Delta W/U = 1.15, \tag{3}$$

where U is the intradonor Coulomb interaction or Hubbard U. The calculations are performed assuming that the impurities are distributed over a regular lattice [simple cubic (sc), bcc and diamond] averaging these different arrangement of the impurities.

(ii) The second is with a randomlike distribution of donors with the probability that the nearest donor neighbor lies at a distance R. Equation (1) is rewritten as[5]

$$\Delta W = 2|\langle T\rangle|, \tag{4}$$

where $\langle T\rangle$ is the average hopping energy integral. It is given by

$$\langle T\rangle = \int T(R) P_\lambda(R) dR, \tag{5}$$

where $P_\lambda(R)$ is the convoluted pair distribution function to be chosen.[31] We use Poisson nearest-neighbor approximation, PNN(R), and Rosso (interaction hierarchy model), PR(R), distributions,[31,32] respectively, as

$$P_{\mathrm{NN}}(R) = \frac{3R^2}{R_d^3} \exp\left(-\frac{R^3}{R_d^3}\right) \tag{6}$$

and

$$P_R(R) = \frac{3R^2}{R_d^3}\left(1+\frac{R^3}{R_d^3}\right)^{-1}, \tag{7}$$

where $R_d = (4\pi N_d/3)^{-1/3}$ and N_d is the donor impurity concentration. The transition is obtained by Eq. (3).

(iii) The third method is by applying a disordered one-band model with many-valley effects.[28] The criterion for the

[a)]Previous address: Instituto de Fisica, UFBa, 40210 Salvador, Ba., Brazil.
[b)]Permanent address.

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MNM transition is also given by Eq. (3), but ΔW is calculated from a random system. The impurity bandwidths are calculated from the equation

$$\xi^{\pm}=E'_{\pm}\overline{G_{ii}^{(\pm)}(E)}, \tag{8}$$

where the bar denotes the configuration averaging of the Green's functions over the random distribution of impurities. For more details the reader should refer to Refs. 1, 28, and 33. In Eq. (8) $E'_{\pm}=E\pm i\epsilon$ and $\xi^{\pm}$ satisfies

$$E'-\frac{E'}{\xi}=\frac{\gamma}{(2\pi)^3}\int\frac{T(\mathbf{k},E')}{1-(N_d\xi/E')T(\mathbf{k},E')}+1+E', \tag{9}$$

where $T(\mathbf{k},E')$ is the Fourier transform of Eq. (2). Here we have taken one of the equivalent minima as the center of k coordinates and neglected the overlap.[28,34] γ is the number of equivalent minima. The coupled equations derived from this scheme are written as[28]

$$P\cos\theta=1+\frac{x_0N_d}{(2\pi)^3}\int T(\mathbf{k},E')[1+x_0\cos\theta T(\mathbf{k},E')]^2\times\frac{d\mathbf{k}}{A(\mathbf{k},E')} \tag{10}$$

and

$$P=\frac{x_0N_d}{(2\pi)^3}\int[T(\mathbf{k},E')]^2\frac{d\mathbf{k}}{A(\mathbf{k},E')}, \tag{11}$$

where

$$A(\mathbf{k},E')=[1+x\cos\theta T(\mathbf{k}_0,E')]^2+[x\sin\theta T(\mathbf{k}_0,E')]^2, \tag{12}$$

$$P=N_da^{*3}, \tag{13}$$

and a^* is the effective Bohr radius.

In the above equations we have used the definition

$$X=-\frac{P\xi}{E'}=x_0\exp(i\theta),\quad 0\leqslant\theta\leqslant\pi. \tag{14}$$

Solving Eqs. (10) and (11) self-consistently for $\theta=0^+$ and $\theta=\pi^-$ we obtain the bandwidths.

(iv) The fourth method is to use a disordered two-Hubbard-bands model.[35] In this model we use the criterion for the transition when the two impurity bands touch each other. The scheme used is the same is in (iii), but for the Hamiltonian

$$H=\sum_{ija}T_{ij}a_{i\sigma}^{+}a_{j\sigma}+\frac{U}{2}\sum_{ija}n_{i\sigma}n_{i-\sigma}. \tag{15}$$

Here $a_{i\sigma}^{+}$ and $a_{j\sigma}$ are the creation and annihilation operators of an electron of spin σ at the impurity site i and $n_{i\sigma}=a_{i\sigma}^{+}a_{i\sigma}$.

The calculated values for the critical concentration N_c of Si:Bi are reported in Table I. For comparison, the values calculated for Si:P are

N_c (Poisson)

$=N_c$ (lattice averaging)$=3.6\times10^{18}$ cm^{-3}.

The experimental value is 3.7×10^{18} cm^{-3}.[1,6,7,13]

TABLE I. The critical concentration N_c for Si:Bi.

E_I (meV)	a^* (Å)	N_c (10^{19} cm^{-3})
69[a,b]	8.7[c]	0.8[a]
		1.7[d]
71[e,f]	8.9[c]	1.8[g]
		1.8[h]
		2.9[i]
		1.1[j]
		1.0[k]
		1.4[l]

[a]Reference 15.
[b]Reference 17.
[c]Effective Bohr radius a^* from the experimental ionization energy E_I: $a^*=e^2/2kE_I$, k is the dielectric constant.
[d]Reference 18; here $k=12$, as in Reference 15.
[e]Reference 16.
[f]Reference 19.
[g]Present calculation, Sec. II, method (i).
[h]Present calculation, Sec. II, method (ii), Poisson distribution.
[i]Present calculation, Sec. II, method (ii) Rosso distribution.
[j]Present calculation, Sec. II, method (iii).
[k]Present calculation, Sec. II, method (iv).
[l]Average of $g+h+j+k$.

III. ELECTRICAL CONDUCTIVITY

The low-temperature impurity dc conductivity is calculated making use of the following equation:[1]

$$\sigma=\frac{e^2\gamma}{3\hbar}\int\sum[E,\xi,T(\mathbf{k}),N_d]\left(\frac{df(E)}{dE}\right)dE, \tag{16}$$

where $f(E)$ is the Fermi distribution function and γ is the number of valleys of the silicon conduction band ($\gamma=6$).[1] It is worth noticing that in deriving the ensemble average of Σ, we are required to calculate the average of a product of two Green's functions as

$$\overline{G_{ij}(E)G_{kl}(E)}\cong\overline{G_{ij}(E)}\;\overline{G_{kl}(E)}. \tag{17}$$

This means that, in this approach, certain terms, arising from the correlated diagrams of the two Green's functions, are neglected. As a consequence, our scheme works fairly well above N_c.[1]

The results for different systems are shown in Fig. 1. For Si:P we also normalize the conductivity to Mott's characteristic minimum conductivity $\sigma_m\approx20$ $(\Omega\,\text{cm})^{-1}$.[6,7] The concentration is normalized to N_c. The values of N_c for the systems are N_c(Si:Sb)$\cong3.0\times10^{18}$ cm^3, N_c(Si:P)$\cong3.7\times10^{18}$ cm^{-3}, N_c(Si:As)$\approx8.5(6.4)\times10^{18}$ cm^{-3}, and N_c(Si:Bi) $\approx1.4\times10^{19}$ cm^{-3}.[1,7,10,20] We obtain the order N_c(Bi) $>N_c$(As)$>N_c$(P)$>N_c$(Sb).[12] The results for Si:P and Si:As present a fairly good agreement with experiments.[3,7,36]

The conductivity as a function of normalized N/N_c obeys the order σ(Bi)$>\sigma$(As)$>\sigma$(P)$>$(Sb). Neglecting the normalization N/N_c and taking $\sigma(T\approx2\text{ K})$ (Ref. 1) as a function of a given impurity concentration, i.e., $N=1.1\times10^{19}$ cm^{-3}, we obtain their values in Table II for different systems. We observe that σ(Sb)$>\sigma$(P)$>\sigma$(As)$>\sigma$(Bi). It is the order found in experiments for σ as a function of $N>10^{19}$ cm^{-3} at room temperature.[36–39]

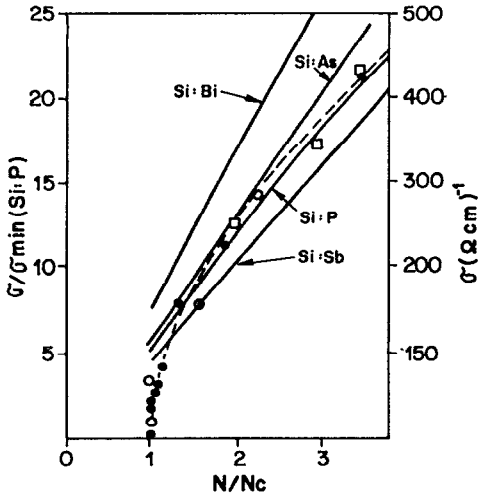

FIG. 1. Electrical conductivity σ of Si:Sb, Si:P, Si:As, and Si:Bi as a function of the normalized impurity critical concentration N/N_c. $\sigma_{\min}$ is Mott's characteristic conductivity. Open and solid circles and open squares are experimental data extracted from Ref. 7.

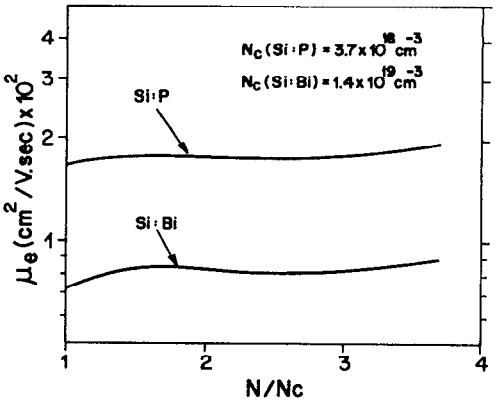

FIG. 2. Mobility of conduction electrons μ_e as a function of N/N_c for Si:P and Si:Bi.

IV. MOBILITY

The mobility of conduction electrons μ_e is extracted from the classical paper of Pearson and Bardeen.[2] It is written as

$$\mu_e = \frac{\sigma}{eN_d} \text{ cm}^2/\text{V s}, \tag{18}$$

where σ is the impurity conductivity, given by Eq. (16), e is the electronic charge, and N_d is the donor concentration. In Fig. 2 we show the mobility for Si:P and Si:Bi as a function of N/N_c. We can observe that for this range of concentration the results present a rough agreement with experiments.[4,25] For Si:Bi Baron *et al.*[25] have found Hall mobility μ_H instead. For the concentration presented here Mousty and co-workers[4] have found that $\mu_H \approx \mu_e$. We obtain a μ_e at a lower value than other systems.

V. SUMMARY

We have reported calculations for MNM transition, electric conductivity, and mobility of conduction electrons of n-doped semiconductors, with emphasis on the Si:Bi system. The schemes presented here show fair agreement when compared to available experimental data for Si:P and Si:As. Experimental and theoretical investigations on Si:Bi system are called for to further check the above studies.

TABLE II. Low-temperature conductivity at $N_d \approx 1.1\times10^{19}$ cm^{-3}.

System	σ (Ω cm)$^{-1}$	
	Theor.	Expt.
Si:Sb	~400	···
Si:P	350	~350[a]
Si:As	140	~150[b]
Si:Bi	120	···

[a]Reference 7.
[b]Reference 36.

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