

Impurity resistivity of the double-donor system Si:P,Bi

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The electrical resistivity of the shallow double-donor system Si:P,Bi, prepared by ion implantation, was investigated in the temperature range from 1.7 to 300 K. Good agreement was obtained between the measured resistivities and resistivities calculated by a generalized Drude approach for the same temperatures and dopant concentrations. The critical impurity concentration for the metal-nonmetal transition for the double-doped Si:P,Bi system was found to lie between the critical concentrations of the two single-doped systems, Si:P and Si:Bi. [S0163-1829(99)11747-8]

I. INTRODUCTION

Double-doped semiconductors continue to be a subject of interest in the physics of disordered materials. In addition to the disorder due to the random spatial distribution of the dopant atoms, there is additional disorder in these systems associated with the different impurity ionization energies of the two dopant elements. In their pioneering investigation of a double-donor system, Newman and Holcomb¹ used conductivity measurements to determine the critical concentration for the metal-nonmetal (MNM) transition in Si:P,As. They showed that, rather than shifting to a higher value due to the additional energy disorder introduced by the double doping, the critical concentration occurs instead at the same reduced concentration as the two single donor materials, Si:P and Si:As.

Silicon doped with bismuth is of particular interest because of its much larger ionization energy (smaller effective Bohr radius) compared to that of other group-V elements (P, As, and Sb)^{2,3}. Bearing in mind the recent investigation on transport properties of Si:Bi,³ we investigate in this work the resistivity of the double donor system Si:P,Bi from room temperature down to 1.7 K for impurity concentrations ranging from the insulating to the metallic range.

The samples were prepared by ion implantation in van der Pauw⁴ structures delineated in Si chips. Ion implantation is an essential process for the fabrication of electronic devices and integrated circuits.⁵⁻⁸ The resistivities obtained experimentally are compared with resistivity values calculated from a recently proposed generalized Drude approach^{3,9} (GDA) for single-doped systems, and here extended to double-doped systems at similar temperatures and dopant concentrations. The impurity critical concentration N_c for the MNM transition is estimated from these results and calcu-

lated using the dielectric function model with a Lorentz-Lorenz correction.

II. EXPERIMENTAL DETAILS

Silicon wafers of *p*-type and (100) orientation with room-temperature resistivities in the range of 11–25 Ω -cm were used for the fabrication of van der Pauw devices. The ohmic contact to the devices were phosphorus doped with low sheet resistance (15 Ω /□).

Multiple implantation steps of Bi and P ions were accumulated in the devices in order to create similar plateaulike concentration depth profiles for Bi and P atoms, extending from the surface to a depth of 0.25 μ m, with an estimated deviation of \approx 5 percent. The doses and energies of the implantation steps were determined from TRIM simulation. All the implants were carried out at nominal room temperature with the sample surface normal tilted at 7° with respect to the direction of incidence of the beam in order to minimize channeling effects. The implantation steps were performed sequentially from the highest to the lowest energy, with the Bi⁻ implants made prior to those of P⁺. Van der Pauw devices with donor atom concentrations (N_d) at the plateaus of 1×10^{20} , 5×10^{19} , 1.0×10^{19} , 8×10^{18} , 7×10^{18} , 6×10^{18} , 4×10^{18} , and 5×10^{17} cm⁻³ were prepared. For N_d of 1×10^{20} cm⁻², i.e., superposed plateaus of 5×10^{19} of Bi and 5×10^{19} cm⁻² of P, the following implantation steps were performed to the doses and energies, respectively of:

(a) Bi⁺ at 4.9×10^{14} cm⁻²/900 keV; 2.9×10^{14} cm⁻²/550 keV; 2.0×10^{14} cm⁻²/360 keV; 1.5×10^{14} cm⁻²/200 keV; 8.0×10^{13} cm⁻²/120 keV; 7.0×10^{13} cm⁻²/70 keV; 5.0×10^{13} cm⁻²/35 keV; and:

(b) P⁺ at 7.0×10^{14} cm⁻²/180 keV; 2.7×10^{14} cm⁻²/120 keV; 1.8×10^{14} cm⁻²/80 keV; 1.5×10^{14} cm⁻²/55 keV;

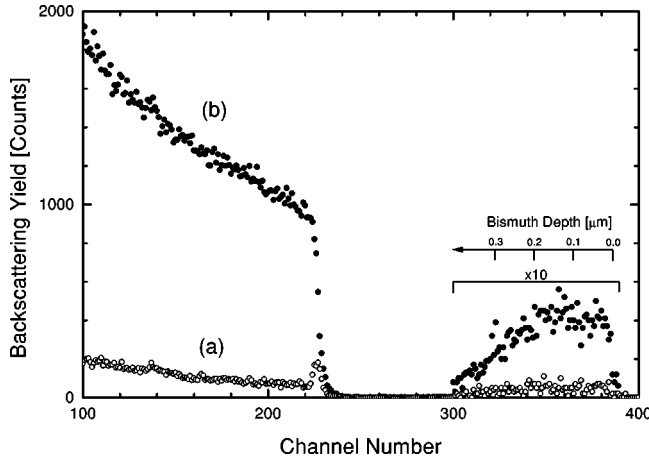


FIG. 1. Rutherford backscattering (RBS) spectra of the sample implanted to the highest dose ($N_d = 1.0 \times 10^{20} \text{ cm}^{-3}$) of Bi and P ions before (curve b) and after (curve a) annealing.

$1.1 \times 10^{14} \text{ cm}^{-2}/30 \text{ keV}$; $6.0 \times 10^{13} \text{ cm}^{-2}/15 \text{ keV}$.

The plateaus with N_d lower than $1 \times 10^{20} \text{ cm}^{-3}$ were prepared using the same energies mentioned above but with the doses reduced by a factor of $N_d/1 \times 10^{20}$. The devices were annealed in an inert atmosphere at 600°C for 15 min followed by rapid thermal annealing at 950°C for 15 s. The samples were analyzed by Rutherford backscattering spectrometry (RBS) using a 1.2 MeV He^+ beam in random and in $\langle 100 \rangle$ aligned (RBS/C) incidence directions.

A resistance bridge was used to measure the resistance of the van der Pauw devices in a ^4He cryostat where sample temperature was controlled between 1.7 K and 300 K. The resistivity was calculated using the expression⁴

$$\rho = \frac{\pi t}{2 \ln 2} (R_1 + R_2) f\left(\frac{R_1}{R_2}\right).$$

Here t is the thickness of the sample, and R_1 and R_2 are the resistances of two van der Pauw configurations, one rotated by 90° relative to the other. The van der Pauw function $f(R_1/R_2)$ satisfies

$$\left(\frac{R_1 - R_2}{R_1 + R_2}\right) = \frac{f(R_1/R_2)}{\ln 2} \operatorname{arccosh}\left[\frac{\exp[\ln 2/f(R_1/R_2)]}{2}\right].$$

For the present samples, $R_1/R_2 \approx 1$, so that the function $f(R_1/R_2)$ can be approximated by

$$f\left(\frac{R_1}{R_2}\right) = 1 - \left(\frac{R_1 - R_2}{R_1 + R_2}\right)^2 \frac{\ln 2}{2}.$$

III. RESULTS

Figure 1 shows the RBS spectra of an annealed sample which has been implanted to the highest doses of Bi and P ions ($N_d = 1 \times 10^{20} \text{ cm}^{-3}$). For better visualization, the spectra for backscattering yield of the Bi atoms were multiplied by a factor of 10. The backscattering of P atoms is not apparent since these spectra overlap those of Si atoms. The following features are disclosed from the RBS and RBS/C spectra (respectively, Rutherford Backscattering Spectrometry and RBS with beam aligned to the $\langle 100 \rangle$ channel): (i)

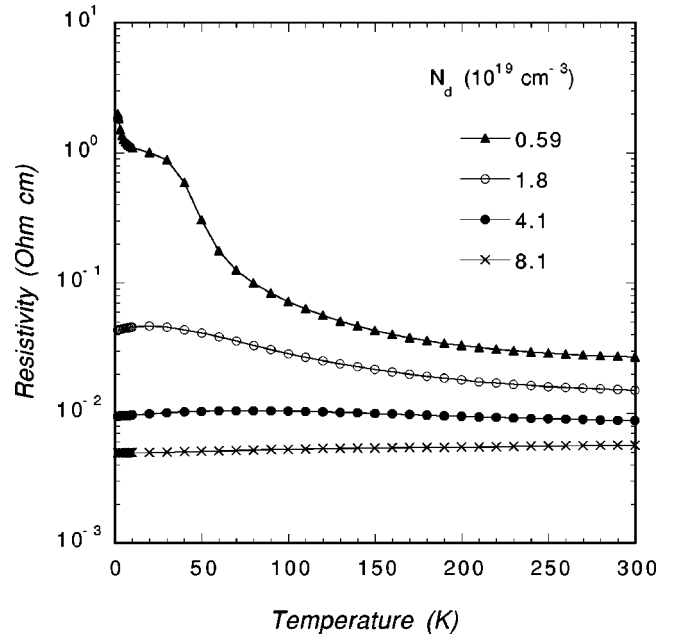


FIG. 2. Temperature dependence of the resistivity of Si:Bi with different donor impurity concentrations N_d .

the residual defect concentration in the implanted Si layer is below the sensitivity of the analysis [see Si backscattering yield in curve (a)], (ii) as predicted by TRIM simulation, the Bi concentration depth profile is a plateaulike shape with $5 \times 10^{19} \text{ cm}^{-3}$ level and depth of $0.25 \mu\text{m}$ [see Bi backscattering yield in curve (b)], (iii) a high substitutional concentration of Bi is clearly apparent [compare Bi backscattering yields in curves (b) and (a)]. The spectra of samples with lower N_d (not shown) present features similar to those described above.

Figures 2 and 3 show the measured resistivity ρ of the

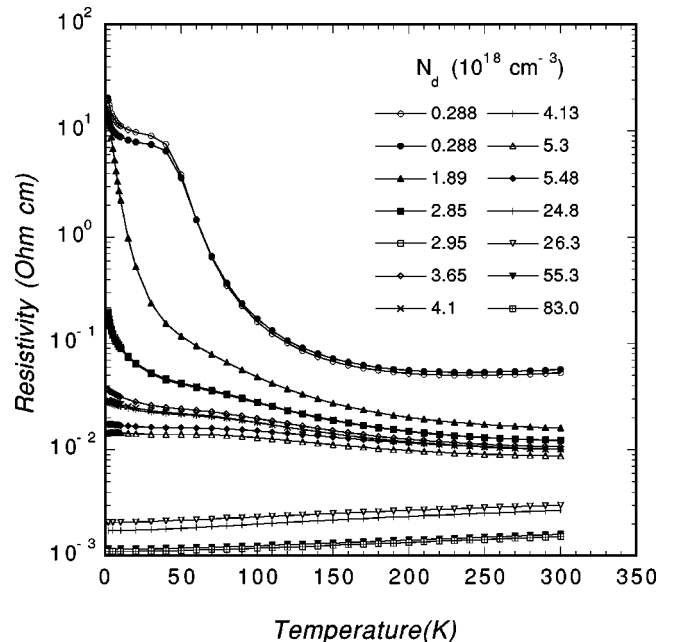


FIG. 3. Temperature dependence of the resistivity of the double-doped system Si:P,Bi with different donor impurity concentrations N_d .

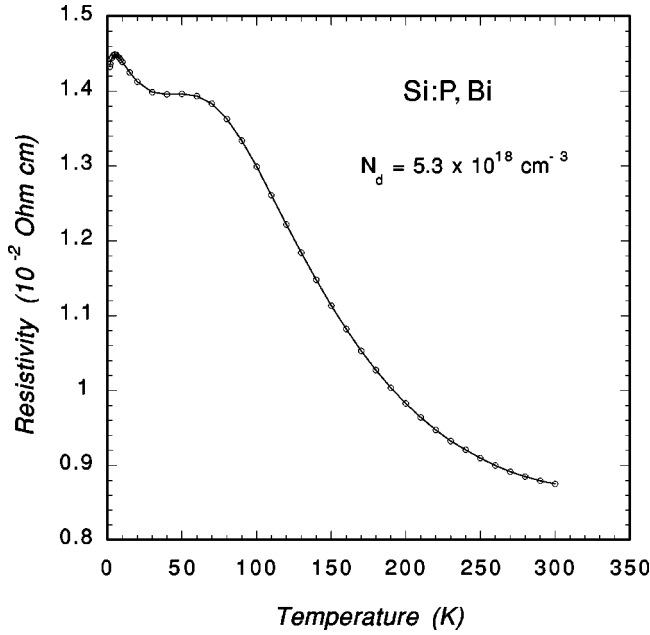


FIG. 4. The resistivity of the Si:P,Bi sample with $N_d = 5.3 \times 10^{18} \text{ cm}^{-3}$ as a function of temperature.

Si:Bi and Si:P,Bi systems, respectively, with different donor impurity concentrations N_d as a function of temperature. One notices similarities between them. The curves for high impurity concentrations shown at the bottom of the figures clearly display metallic character.

For Si:P,Bi, which is the main object of our interest here, Fig. 3 shows the slope of the resistivity curves decreasing with increasing impurity concentration in the region of low temperature down to our lowest temperature, 1.7 K, leading to a smooth decrease in $\rho(T)$ when a MNM transition is expected.

In Figs. 4 and 5 we show the temperature dependence of the resistivity for $N_d = 5.3 \times 10^{18}$ to $2.63 \times 10^{19} \text{ cm}^{-3}$, corre-

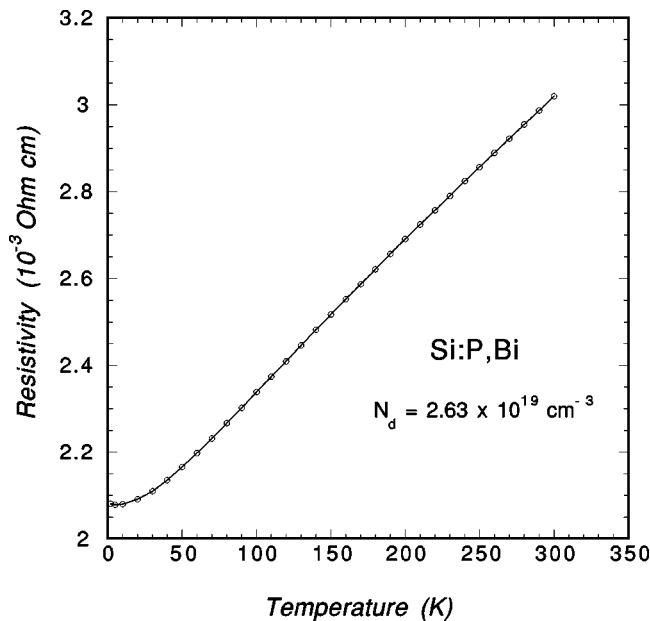


FIG. 5. The resistivity of the Si:P,Bi sample with $N_d = 2.63 \times 10^{19} \text{ cm}^{-3}$ as a function of temperature.

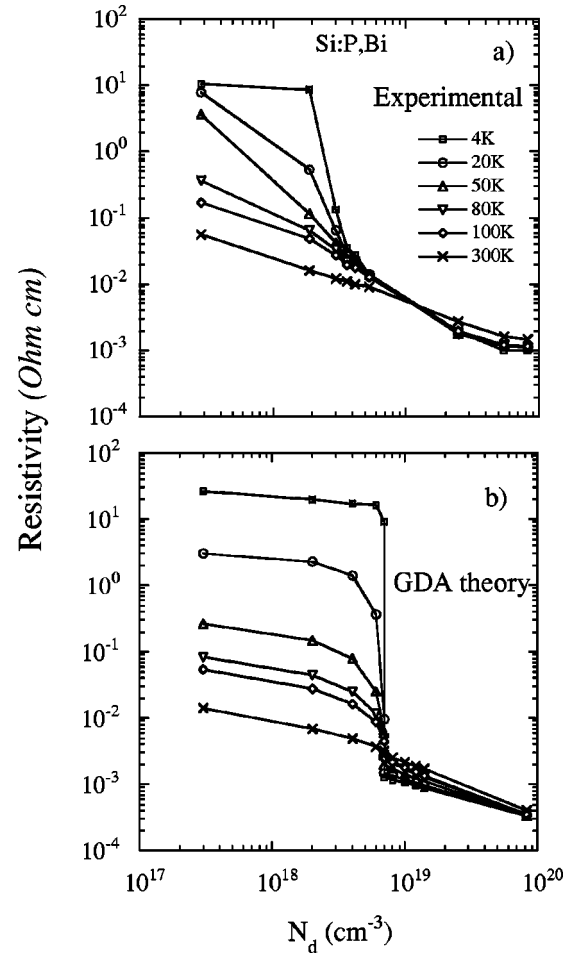


FIG. 6. Resistivity of Si:P,Bi samples as a function of the donor impurity concentration N_d (a) measured and (b) calculated by the generalized Drude approach at different temperatures.

sponding to the region of densities where the MNM transition of Si:P,Bi is expected to occur.

Figure 6(a) shows the dependence of the resistivity of Si:P,Bi on the donor impurity concentration N_d at different temperatures. One notices that all the curves merge together to one critical point. Figure 6(b) shows the theoretical resistivity calculated from the generalized Drude approach in the same range of donor concentrations and at the same temperatures as Fig. 6(a). The calculation using the GDA method and the determination of the critical concentration of Si:P,Bi are described in the next section.

IV. THEORY AND DISCUSSION

Following the previous calculations³ that use the GDA method to determine the resistivity and the critical concentration of the shallow single-donor system Si:Bi, we have extended these calculations to double-doped systems, with application to Si:P,Bi. For the resistivity calculations, the results depend on the degree of ionization of the donors. In the metallic region we assume that all donors are ionized. For finite temperatures there are always some ionized donors even on the insulating side of the critical concentration and the density of unionized donors N_u differs from the density of donors N_d . The carriers released should contribute to the

screening and further reduce the ionization energy, introducing a temperature-dependence, which we will neglect. Assuming that the concentration of each dopant is given by $N_d = N_{d,1} + N_{d,2}$, we calculate the energy of the two resulting modes, $E_{I,i}$ and the relative weights χ_i . The imaginary part of the inverse of the dielectric function in Eq. (8), below, has two peaks corresponding to excitations from the two levels. The relative weights are defined as the relative areas of the two peaks. Some of the dopants will be ionized, N , and the rest are unionized. The density of free carriers, in the non-metallic regime, is determined from simultaneously solving the following equations

$$N_d = N_u + N \quad (1)$$

$$N_u = N_d \left\{ \frac{\chi_1}{e^{[E_{I,1} - \mu(N,T)]\beta} + 1} + \frac{\chi_2}{e^{[E_{I,2} - \mu(N,T)]\beta} + 1} \right\}$$

where $E_{I,i}$ ($i=1,2$) is the ionization energy for a single donor of type i , $\beta = 1/k_B T$, k_B is Boltzmann's constant and $\mu(N,T)$ is the chemical potential. The model is then presented with two localized donor levels below the conduction band. The carriers are distributed among these levels and the continuum states according to the Fermi-Dirac distribution function.

For nonpolar semiconductors the generalized Drude approach for the resistivity is reduced to^{2,3,9-11}

$$\rho(\omega) = \frac{-im^*\omega}{Ne^2} + \frac{i2}{3\pi N\omega} \int_0^\infty q^2 \left[\frac{1}{\varepsilon_T(q,\omega)} - \frac{1}{\varepsilon_T(q,0)} \right] dq, \quad (2)$$

where e is the electric charge, m^* is the effective mass, and ε_T is the total dielectric function. We have assumed a random distribution of Coulomb impurities. The total dielectric function is given by¹⁰

$$\varepsilon_T(q,\omega) = \varepsilon + v\alpha_1(q,\omega) + i v\alpha_2(q,\omega), \quad (3)$$

where ε is the dielectric constant for Si and α_1 and α_2 are the real and imaginary parts of the polarizabilities from one of the v valleys of dopant carriers. The number of valleys is 6, $\varepsilon = 11.4$ in Si, and these functions are temperature dependent. The imaginary part can be obtained analytically in the random phase approximation.¹² It is given by

$$\begin{aligned} \alpha_2(Q,W) &= - \frac{m^*e^2}{8\hbar k_F Q^3 B} \\ &\times \left[\ln \left(\frac{\cosh\{B[W + (Q^2 + W^2/Q^2 - M)/2]\}}{\cosh\{B[W - (Q^2 + W^2/Q^2 - M)/2]\}} \right) - 2BW \right], \end{aligned} \quad (4)$$

where we have introduced the dimensionless variables $Q = q/2k_F$, $W = \hbar\omega/4E_F$, $B = \beta E_F$, and $M = \mu/E_F$. The quantity k_F is the Fermi wave vector, given by $k_F = (3N\pi^2/v)^{1/3}$, and E_F is the Fermi energy. The real part can be obtained from the imaginary part through the Kramers-Kronig dispersion relation.

We are interested in the static resistivity, which can be written as

$$\rho(0) = \frac{16\hbar k_F^3 v}{12\pi N E_F} \int_0^\infty Q^2 \frac{[\partial\alpha_2(Q,W)/\partial W]|_{W=0}}{[\varepsilon + v\alpha_1(Q,0)]^2} dQ, \quad (5)$$

which can be reduced to

$$\rho(0) = \frac{2v(m^*e)^2}{3\pi N\hbar^3 k_F} \int_0^\infty \frac{\{1 - \tanh[0.5B(Q^2 - M)]\}}{Q[\varepsilon + v\alpha_1(Q,0)]^2} dQ. \quad (6)$$

The chemical potential μ is obtained from the implicit expression^{3,11,13}

$$B^{3/2} = \int_0^U \frac{3y}{1-y^2} \{A + \ln[(1-y^2)/y^2]\}^{1/2} dy, \quad (7)$$

where $U = (1 + e^{-A})^{-1/2}$ and $A = BM = \mu B$. For a given A , one obtains B leading to a relation between them.

The calculated resistivity of Si:P,Bi as a function of impurity concentration and temperature obtained using the procedure described above is presented in Fig. 6(b) and compared to the measured resistivity shown in Fig. 6(a). Both measured and calculated resistivity curves present similar forms, converging to a value around $6.0 \times 10^{18} \text{ cm}^{-3}$, which is determined to be the critical concentration N_c for the MNM transition in Si:P,Bi. For the measured resistivity at 300 K we observe a small difference compared to the other ones. For impurity concentrations in the metallic region, i.e., above N_c , the temperature dependence of the resistivity is negligible in comparison with the nonmetallic region.

The ionization energies $E_{I,i}$ for the double-doped systems are determined using the Lorentz expression for the dielectric function but with the Lorentz-Lorenz correction and two ionization energies. The dielectric function for silicon plus unionized donors is

TABLE I. Theoretical (t) and experimental (e) results for the critical concentration N_c for the MNM transition.

System	E_I (meV)	N_c^t (10^{18} cm^{-3})	N_c^e (10^{18} cm^{-3})
Si:Bi	71.00	16.90	$\sim 20.00^a$
Si:As	53.60	7.26	8.50^b
Si:P	45.44	4.42	3.48^d
			3.75^c
Si:P,Bi		7.00	$\sim 6.00^e$
		$\sim 6.00^f$	
Si:P,As		5.49	5.10^g

^aFrom Ref. 3.

^bFrom Ref. 14.

^cFrom Ref. 15.

^dFrom Ref. 16.

^eFrom Fig. 6(a).

^fFrom Fig. 6(b).

^gFrom Ref. 1.

$$\varepsilon(\omega) = 1 + \frac{\frac{4\pi N_{u,1}\alpha_{d,1}\omega_{0,1}^2}{\omega_{0,1}^2 - \omega^2 - i\Gamma_1\omega} + \frac{4\pi N_{u,2}\alpha_{d,2}\omega_{0,2}^2}{\omega_{0,2}^2 - \omega^2 - i\Gamma_2\omega} + 4\pi N_h\alpha_h}{1 - \frac{1}{3} \left(\frac{4\pi N_{u,1}\alpha_{d,1}\omega_{0,1}^2}{\omega_{0,1}^2 - \omega^2 - i\Gamma_1\omega} + \frac{4\pi N_{u,2}\alpha_{d,2}\omega_{0,2}^2}{\omega_{0,2}^2 - \omega^2 - i\Gamma_2\omega} + 4\pi N_h\alpha_h \right)}, \quad (8)$$

where $\alpha_{d,i}$ is the static polarizability for a single donor of type i in the silicon matrix, α_h is the contribution from the static polarizability for the host, $N_{u,i}$ the density of unionized donors, N_h is the contribution of the host charge density and $E_{0,i} = \hbar\omega_{0,i}$ is the ionization energy for a single donor of type i . Following a procedure similar to that used in Ref. 3, the denominator of the dielectric function has two zeros, corresponding now to the two ionization energies. As the donor concentration increases, one of the ionization energies eventually vanishes. This defines the critical concentration. The calculated and experimental values of MNM transitions are presented in Table I.

V. SUMMARY

We have reported results of an experimental and theoretical investigation of the impurity resistivity of the ion-implanted double-donor system Si:P,Bi from room tempera-

ture down to 1.7K for concentrations spanning the insulating to the metallic regimes. Good agreement with the experimental results were obtained from calculations using a generalized Drude approach. The value of the impurity critical concentration N_c for the MNM transition was estimated from both methods above as well as through the dielectric function with the Lorentz-Lorenz correction. The critical impurity concentration N_c for the double-doped Si:P,Bi system was found to be intermediate between the critical concentrations of the two single-doped systems, Si:P and Si:Bi.

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