Metal-Insulator Transition in a Double-Donor System, Si:P,As

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Measurements of electrical conductivity σ as a function of temperature in the double-donor system Si:P,As are reported. Data are related to a reduced concentration variable which is defined in terms of space filling by the interwoven impurity systems. The metal-insulator transition, when compared with those in Si:P and Si:As, appears to be unaffected by the additional vertical disorder introduced by the differing ionization energies of the two donors.

The transition from semiconducting to metallic behavior in Si and Ge which is produced by increasing donor or acceptor concentrations has been studied for many years. The essential idea that increasing overlap of wave functions of bound impurity charges can lead to carrier delocalization was understood from the beginning.[1] But development of a satisfactory theoretical model to represent the exact form of the electrical transport properties as a function of composition and temperature has been a surprisingly long process. In particular, it has been very difficult to separate from one another effects caused by the intrinsic disorder in the randomly placed impurity atoms and effects stemming from screening, correlation, and other electron-electron interaction effects.

In order to achieve more independent control of relevant parameters, we set out to study silicon containing two different donors with differing values of the impurity ionization energy, E_I. We introduce the two donors for the purpose of increasing vertical disorder in the impurity system, without altering electron-electron interaction effects in any significant way. We report here results on the first of these double-donor systems, Si:P,As. Values of E_I for isolated P and As donors in Si are 45 and 53 meV, respectively.[2] The difference, 8 meV, is much larger than our estimated width of the distribution of single-site binding energies for either of the single-donor systems, Si:P and Si:As, at concentrations of interest. The root second moment of this distribution, calculated on the basis of a first-order tight-binding model, is about 2 meV. Our results show that the value of the critical composition for the M-I transition in the double-donor system is consistent with predictions of a geometrical, space-filling model, and is not shifted to significantly higher impurity concentration by the additional vertical energy disorder introduced by the double doping.

Figure 1 shows our data for $\sigma(T)$ from samples whose characteristics are given in Table I. Samples were cut from wafers sliced from a Czochralski-grown, double-doped boule.[3] Sample preparation and measurement systems were identical to those described in a recent paper from our laboratory which gives results in the single-donor system Si:As.[4] The scale of values of As concentration, n_{As}, has been determined by neutron activation analysis.[5] Values of total donor concentration, $n_P + n_{As}$, are derived from measured values of room-temperature resistivity, with use of the calibration scale given by Thurber et al.[6] for Si:P. Our neutron activation measurements in Si:As show that this resistivity calibration scale, when used for As donors with concentrations near 10^{19} cm^{-3}, gives values of n_{As} which are about 9% too small. But the deviation between P and As shrinks as n_{As} approaches 10^{18} cm^{-3}, and this calibration scale is correct for
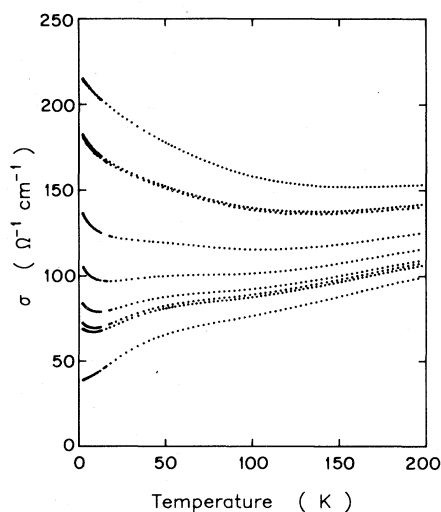

FIG. 1. The dc conductivity of Si:P,As samples as a function of temperature. Composition of the samples is given in Table I. The data curves, reading from bottom to top, match samples A through I sequentially.

TABLE I. Characteristics of Si:P,As samples.

Sample	ρ(296 K) (10^{-3} Ω cm)	$n_P + n_{As}$ [a] (10^{18} cm^{-3})	n_{As} [b] (10^{18} cm^{-3})	$\sigma(0)$ (Ω^{-1} cm^{-1})	m (Ω^{-1} cm^{-1} K$^{-1/2}$)
A	9.01	5.35	2.14	36.0	-1.9
B	8.57	5.78	2.38	70.9	-1.7
C	8.46	5.90	2.45	75.5	-2.6
D	8.17	6.22	2.63	88.6	-3.7
E	7.95	6.48	2.77	113.0	-5.5
F	7.54	7.01	3.07	144.5	-6.1
G	7.06	7.71	3.46	192.0	-6.4
H	6.81	8.11	3.69	189.2	-5.2
I	6.44	8.77	4.06	221.3	-4.7

[a] Absolute values ± 6%, relative values ±2%.
[b] Absolute values ± 3%, relative values ±2%.

our samples, within an estimated 5% uncertainty.

In order to analyze the data given in Fig. 1, we first obtain a zero-temperature value of conductivity, $\sigma(0)$, by extrapolating the curves of Fig. 1 to $T = 0$ with a fitting function $\sigma(T) = \sigma(0) + mT^{1/2}$. We note that there is theoretical justification for the use of this function.[7] Values of $\sigma(0)$ and m from these fits are given in Table I.

For Si:P [8] or Si:As,[4] a plot of $\sigma(0)$ as a function of donor concentration, n_P or n_{As}, yields a curve which characterizes the M-I transition. For Si: P,As we introduce a reduced concentration variable, η, given by the defining equation

$$\eta = n_P/(n_c)_P + n_{As}/(n_c)_{As}.$$

We will show that use of this quantity provides a simple and revealing analysis scheme.

The definition of η rests on the realization that the random overlapping of impurity-atom wave functions must play a role in establishing the value of the critical composition. Motivated by this realization, we draw on some ideas developed in percolation theory. In a simple model of overlapping spheres of a single radius, the critical volume fraction occupied by the spheres at the percolation threshold is independent of the sphere size. Our definition of reduced concentration, η, is based on the strong intuition that for a system composed of spheres of differing sizes, the critical volume fraction (CVF) at percolation will have the same value as for the single-radius case. In a Monte Carlo calculation[9] Pike and Seeger have shown that this statement is closely true when they compare the value of the CVF at percolation for a system of randomly placed, interpenetrating spheres of a single radius (CVF = 0.295) with that for a continuous distribution of radii ranging from $r = 0$ up to some

maximum radius (CVF = 0.303). These ideas lead to the definition of η given above, as we briefly sketch out below.

In a random system of impurities of spherical symmetry with some effective radius, r_i, the fraction of the volume occupied by the impurity system, f_i, uncorrected for overlap, is given by

$$f_i = \tfrac{4}{3} \pi r_i^3 n_i,$$

where n_i is the impurity concentration. At some critical concentration $(n_c)_i$, f_i will have a particular value given by

$$(f_c)_i = \tfrac{4}{3} r_i^3 (n_c)_i = \text{some number, } k. \qquad (1)$$

If two separate impurity systems are similar except that they have different values of the radius, r_i, we expect the value of the constant, k to be the same for the two systems.

For our purposes, we apply this model to the doped Si systems, and take n_c to be the critical concentration for the M-I transition. But it is important to note that we will not need to know the actual value of k, and thus we need not identify r_i with any particular parameter of the impurity atom.

For a system with two sets of spheres, of different radii,

$$f_{12} = (\tfrac{4}{3}\pi r_1^3 n_1 + \tfrac{4}{3}\pi r_2^3 n_2),$$

and

$$(f_c)_{12} = [\tfrac{4}{3}\pi r_1^3 (n_1)_c + \tfrac{4}{3}\pi r_2^3 (n_2)_c] = k, \qquad (2)$$

where the quantities $(n_1)_c$ and $(n_2)_c$ are the concentrations of impurities of types 1 and 2 in the double-doped sample at the critical composition. Note that our quantity, f_c, while related to the CVF, is not exactly that quantity. The value of f_c is larger than CVF because of the effects of

overlap. In the last step of Eq. (2) we have introduced the crucial step noted above, namely, the volume fraction at the critical composition for the double-impurity system is taken to have the same value as for the single-impurity systems. That is, $(f_c)_{12}$ is set equal to k.

We now define the reduced concentration, η, by the relation, $\eta = f/f_c$. Then for a single-donor system $\eta_i = n_i/(n_c)_i$, and for the double-donor system,

$$\eta_{12} = f_{12}/(f_c)_{12} = \frac{k[n_1/(n_c)_1] + k[n_2/(n_c)_2]}{k}$$

$$= n_1/(n_c)_1 + n_2/(n_c)_2. \qquad (3)$$

We have used Eq. (1) to eliminate r_1^3 and r_2^3, and Eq. (2) to replace $(f_c)_{12}$ by k.

Note that the constant, k, drops out of the expression for η_{12}. Therefore, we do not need to make an identification of the critical composition with any particular topological criterion such as formation of the infinite cluster in percolation theory.

We now use the definition of η_{12} in Eq. (3) to locate our samples on the reduced concentration scale shown in Fig. 2. We identify n_1 with n_P and
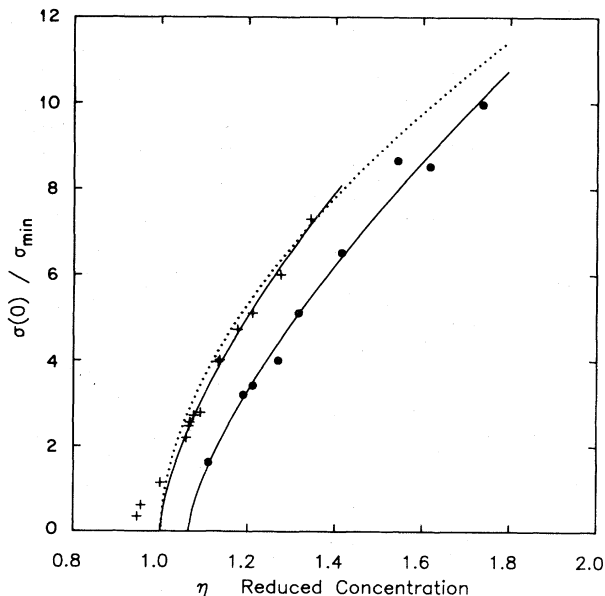

FIG. 2. Normalized dc conductivity, $\sigma(0)/\sigma_{min}$, as a function of reduced concentration, η. The solid dots give values for the nine samples of Si:P, As listed in Table I. The crosses show data for Si:As, taken from Ref. 4. The solid lines are best-fit curves for Si:P, As and Si:As, with use of the fitting function $\sigma(0) = \sigma_0(\eta/\eta_c - 1)^\nu$. The dotted curve, for Si:P, is taken from Ref. 8.

$(n_c)_1$ with the value of n_c for Si:P given by Rosenbaum et al.,[8] 3.74×10^{18} cm^{-3}; n_2 with n_{As} and $(n_c)_2$ with the value of n_c for Si:As,[4] 8.5×10^{18} cm^{-3}.

Figure 2 also includes the data for Si:P and Si:As from Refs. 4 and 8, plotted according to the appropriate reduced concentration. Conductivity values in Fig. 2 are also given in terms of a scaled variable, σ/σ_{min}. The quantity σ_{min} is discussed in Refs. 4 and 8. It has the value 20 Ω^{-1} cm^{-1} for Si:P and 26 Ω^{-1} cm^{-1} for Si:As. Its appropriate value for Si:P, As is 22 Ω^{-1} cm^{-1}.

The fact that curves for both Si:P and Si:As drop to zero at exactly $\eta = 1.0$ follows from the fact that experimental values of n_c were used in establishing the scale of η in the two single-donor systems. But the fact that the curves for Si:P and Si:As closely overlap for values of $\eta > 1.0$ demonstrates the similarity of the conductivity transition in the two systems.

The essential new information from this experiment is contained in the curve for Si:P, As shown in Fig. 2. The value of $(\eta_c)_{P,As}$ is 1.06. It is difficult to make a really good estimate of the experimental uncertainty in this number, because of the complicated way in which errors in determining values of n_{As}, $(n_c)_{As}$, n_P, and $(n_c)_P$ enter into the uncertainty in values of η. Our best estimate[5] of the uncertainty in $(\eta_c)_{P,As}$ is $\pm 7.5\%$. Thus, $(\eta_c)_{P,As} = 1.06 \pm 0.07$, a value indistinguishable from 1.00. To the accuracy we have available, the value of η_c in Si:P, As is just that predicted by the argument that the transition will take place at the same value of the volume fraction of space occupied by the combined impurity system as for each of the single-donor systems.

The solid line in Fig. 2 is a fit of the equation $\sigma = \sigma_0[\eta/\eta_c - 1]^\nu$ with each of the three fitting parameters allowed to vary freely. Table II compares the values of fitted parameters with the values obtained from previous analysis of Si:P and Si:As. There is no measurable difference in the behavior of the double-donor system in comparison to the two single-donor systems and thus, no measurable effects of the additional vertical disorder introduced by the different impurity binding energies.

The form of the dependence of the low-temperature conductivity on impurity concentration closely resembles that previously observed in Si:P and Si:As, but differs from that of other disordered systems, such as Nb:Si.[10] The common behavior of these silicon impurity systems may motivate one to look carefully at recent theore-

TABLE II. Fitting parameters for equation $\sigma(0) = \sigma_0(n/n_c - 1)^\nu$.

System	n_c (cm^{-3})	ν	σ_0
Si:P [a]	$(3.74 \pm 0.2) \times 10^{18}$	0.55 ± 0.1	$13\sigma_{min}$
Si:As [b]	$(8.50 \pm 0.5) \times 10^{18}$	0.65 ± 0.1	$14.5\sigma_{min}$
Si:P, As	5.10×10^{18} [c]	0.7 ± 0.2	$13\sigma_{min}$

[a]Ref. 8.

[b]Ref. 4.

[c]This is the sum, $n_P + n_{As}$, at the transition. In our set of samples, these values are 3.1×10^{18} cm^{-3} and 2.0×10^{18} cm^{-3}, respectively. Since the value of this sum at the transition will depend on the relative concentration, n_P/n_{As}, it is less useful than the value of the reduced concentration, $(\eta_c)_{P, As}$.

tical work by Berggren[11] and by Bhatt and Ramakrishnan.[12] These authors attempt to incorporate both electron-electron interaction effects and effects of disorder into models which might be particularly applicable to the heavily-doped, uncompensated semiconductors.

A comparison of the temperature dependence of the curves in Fig. 1 for 1.8 K $< T <$ 200 K with similar data for Si:As given in Fig. 1 of Ref. 4 shows some noticable differences in the interplay of various scattering mechanisms in the two systems. We suspect that analysis of those differences will be illuminating, but we have not yet had an opportunity to attempt that analysis.

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