

Variation of impurity-to-band activation energies with impurity density*

T. F. Lee[†] and T. C. McGill

California Institute of Technology, Pasadena, California 91109

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A theory of the variation of conduction electron density with the temperature for various impurity concentrations is presented. In addition to previously noted effects of conduction band edge lowering and screening of the impurity potential by the conduction electrons, the influence of a finite energy transfer integral and spatial fluctuation in the potential are included. The results show that for $N_D \gtrsim 10^{17}$ cm⁻³ in silicon one must not view the activation as occurring between a single impurity level and a well-defined conduction band edge, but must include the broadening of the impurity level and tailing of the conduction-band density of states. Calculations for the shallow donors P, Sb, and As in Si are found to be in satisfactory agreement with experiment.

I. INTRODUCTION

Since the work of Pearson and Bardeen,¹ it has been well known that the impurity-to-band activation energy in semiconductors decreases with increasing impurity concentrations. At low impurity concentrations (for example, less than 10^{17} P/cm³ in silicon), the variation of activation energy with impurity concentrations is small. At high impurity concentrations, the activation energy is strongly dependent upon the impurity concentrations. A number of different suggestions have been put forward to account for this phenomenon theoretically. Pearson and Bardeen,¹ and Castellani and Seitz² suggested that the decrease of impurity-to-band activation energy with impurity concentrations was due to attraction between the conduction electrons and ionized donors. Calculations based upon this physical phenomenon yielded qualitative but not quantitative agreement with the experimental results. Pincherle³ proposed that free carriers screen the field of the impurity center and hence decrease the binding energy of a carrier electron to an impurity center. Calculation based on this proposal alone did not give satisfactory results. A self-consistent calculation which combined the two models was given by Lehman and James.⁴ While this calculation was in good agreement with experiment for low impurity concentrations, at high impurity concentrations (10^{16} cm⁻³ shallow donors in Ge), their calculations underestimate the experimentally observed decrease of activation energy. A more systematic treatment proposed by Debye and Conwell⁵ suggested that a correct description would include three effects: (i) lowering of the conduction band edge due to attraction of the conduction electrons by the ionized donors; (ii) the shift of the donor ground-state energy due to free-electron screening; and (iii) the increase in the dielectric constant due to the presence of the polarizable neutral donors. As in the case of Lehman and James, they obtain good agreement. However, none of these authors have considered the influence of effects which broaden the impurity level and, hence, lead to an additional effective shift in the observed activation energy.

In this paper we consider the change in the observed activation energy due to the influence of those effects which both broaden and shift the impurity level. We consider the same phenomenon which tend to shift the level as considered by Debye and Conwell.⁵ We have included

two effects which tend to broaden the level. First, the impurity-level wave function at a given impurity has finite Hamiltonian matrix elements with impurity-level wave functions centered at nearby impurities. This leads to broadening of impurity levels when the impurities are at finite density to produce a band of levels. Second, the presence of charged impurities distributed in a random way throughout the solid generates potential fluctuations. These potential fluctuations produce tailing of conduction- and valence-band density of states⁶ and spreading of impurity levels.⁷ For simplicity, we will confine our attention to shallow donor levels with compensating acceptors in silicon.

This paper is organized in the following fashion. In Sec. II, we consider those phenomena which shift the energy level. In this section, we review the results of Lehman and James and put the formulas in a form suitable for our use. In Sec. III, we consider the tailing of the conduction band edge due to potential fluctuations. In Sec. IV, the phenomena which broaden the impurity level are investigated. Section V contains the calculations of conduction electron concentration n vs temperature T for various donor and compensating acceptor concentrations and compare the calculated results with the known experimental results. Section VI contains a brief discussion and conclusions.

II. IMPURITY-LEVEL SHIFT WITH RESPECT TO CONDUCTION BAND EDGE

In the effective mass approximation, the Hamiltonian for the conduction electrons consists of the kinetic energy of the electrons, electron-impurity Coulomb interactions, and the electron-electron interactions. Once an electron is bound to a donor ion, then the donor ion plus electron becomes a neutral system and has little effect on the motion of conduction electrons. Hence, the unbound electron motion can be accurately described by a Hamiltonian which does not include any interaction with these neutral systems. The motion of conduction electrons can be approximately described by a series of one-electron Hamiltonian^{8,9}

$$H = \frac{p^2}{2m^*} + \sum_{\beta} \frac{Z_{\beta} q^2 \exp[-(|\mathbf{r} - \mathbf{R}_{\beta}|)/\lambda_{\beta}]}{4\pi\epsilon\epsilon_0 |\mathbf{r} - \mathbf{R}_{\beta}|}, \quad (2.1)$$

where \mathbf{r} and p are the position and momentum, respectively, of the electron; \mathbf{R}_{β} is the position of the β th im-

purity which has signed charge Z_B ; the prime above the summation indicates that the sum runs over ionized impurities only. The semiconductor is described by an isotropic effective mass m^* and dielectric constant ϵ . The electron screening length is λ_e . For the nondegenerate case, the electron screening length is given by¹⁰

$$\lambda_e = (\epsilon\epsilon_0 K_B T / q^2 n)^{1/2}, \quad (2.2)$$

where n is conduction electron concentration, K_B is the Boltzmann constant, and T is absolute temperature. For silicon, λ_e ranges typically between 40 and 10^4 Å for $n = 10^{18}$ cm⁻³ and $T = 300$ °K, and for $n = 10^{12}$ cm⁻³ and $T = 50$ °K, respectively. We will use the Hamiltonian in Eq. (2.1) to describe the unbound conduction electrons.

There are several effects which are thought to be related to the shift of impurity levels with respect to the conduction band edge. They are (i) the change of dielectric constant due to the presence of neutral donors, (ii) the influence of conduction electron screening on donor ground-state energy, and (iii) the conduction band edge lowering due to attraction between conduction electrons and ionized donors. In the following, we are going to examine these three effects.

A. Neutral donor polarization

In Eq. (2.1), there is some question about what dielectric constant we should use. As pointed out by Castellani and Seitz,² we should include the contribution to ϵ due to the presence of polarizable neutral donors. However, this produces a small change in ϵ . For donor concentrations up to 10^{18} neutral donors/cm³, the concomitant shift of impurity energy level relative to the conduction band edge is less than 1 meV. Hence, we will assume that the dielectric constant is independent of impurity concentrations.

B. Shift of impurity level due to screening

The presence of the conduction electrons should screen the attractive interaction between the donor ion and the bound electron in a donor level. This screening will shift the energy of the ground state toward the conduction band. Using the Hartree approximation, Lehman and James⁴ treated this effect in their self-consistent calculation. For the purpose of estimating the size of this effect and to separate it from the shift of the conduction band edge, we made a simple first-order perturbation calculation of the influence of screening on this effect. We approximate the donor ground-state wave function by a single 1s Slater orbital with an exponent of ξ . The potential due to the conduction electrons is obtained by computing the change in local electron density due to the presence of the donor ion and the bound electron in a linearized Hartree approximation.

Since the electron screening length is larger than the size of the donor-level wave function, i.e., $\xi\lambda_e > 1$, the difference between the screened ion potential and the unscreened ion potential is small. First-order perturbation theory of this difference potential can be used to estimate the shift. The result of the calculation is

$$\Delta E_B \equiv \frac{q^2 \xi}{4\pi\epsilon\epsilon_0} \left(\frac{3}{8} - \frac{2\xi\lambda_e \sin[(1/2\xi\lambda_e) + 2 \tan^{-1}(1/8\xi\lambda_e)]}{4 + 1/16\xi^2\lambda_e^2} \right). \quad (2.3)$$

The calculations leading to this result are presented in the Appendix. Since ΔE_B is a monotonically decreasing function of the screening length λ_e , we can obtain an upper bound to ΔE_B by taking the smallest value of λ_e that we encountered under the present experimental conditions (about 40 Å). Taking ξ to be the reciprocal of the Bohr radius for the donor ($\xi = 1/19$ Å) in Si, we have

$$\Delta E_B \leq 1 \text{ meV}$$

for conduction electron concentrations less than 10^{18} cm⁻³ in Si. This result agrees with the calculations of Lehman and James which indicated that screening produced a small impurity-level shift. Therefore, we can neglect the effect of screening on the donor ground-state energy level.

C. Average shift of conduction band edge

The presence of ionized donors and compensating acceptors changes the position of the conduction band edge. The random spatial distribution of the ionized centers leads to not only an average shift of the conduction band edge but also spatial fluctuations in the position of the conduction band edge. In this section we concentrate on the average shift of the conduction band edge and leave to a later section the discussion of fluctuations.

To make an estimate of the average shift, we should, in principle, calculate the energy levels associated with the potentials due to the ionized impurities, then devise some method of defining the bottom of the conduction band, and finally average this over all the possible spatial configurations of ionized impurities. While this is, in principle, the way to proceed, in practice we can not carry out such a calculation in anything but the most idealized models. Thus, we proceed by first obtaining a potential which should approximate the potential due to the ionized impurities. In obtaining the potential due to a single ionized donor, the principal dopant, we must note that the Coulomb potential of a donor is modified by the presence of the conduction electrons and also by the increased probability of finding an ionized acceptor near an ionized donor. These two effects are taken into account by screening the Coulomb potential of the donor. The screening length is made up of two parts—that due to the electrons and that due to the ionized impurities. The screening length for the electrons is the same as that given before in Eq. (2.2). The screening length for ionized impurities is given by a standard Debye screening length form (λ_i)^{11,12} modified by the addition of a length which is the average spacing between impurities.⁷ That is,

$$\lambda_i = \lambda_{i0} + a, \quad (2.4)$$

where

$$\lambda_{i0} = \left(\frac{\epsilon\epsilon_0 k_B T / q^2}{(N_A + n)(1 - N_A + n/N_D)} \right)^{1/2}, \quad (2.5)$$

and

$$a = \Gamma\left(\frac{4}{3}\right) \left[\frac{4}{3} \pi (N_D + N_A) \right]^{-1/3}, \quad (2.6)$$

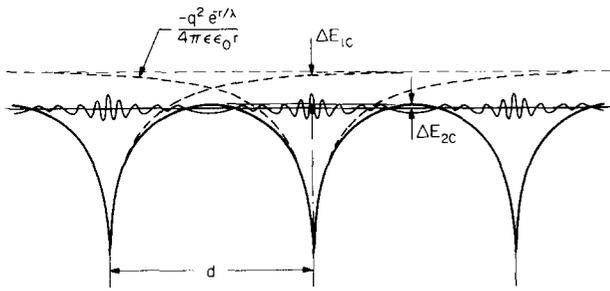


FIG. 1. The shift of conduction-band edge due to overlap of ionized donor potentials. The lowering of barrier height is ΔE_{1c} and the total shift of conduction-band edge is $\Delta E_{1c} + \Delta E_{2c}$.

which is the average distance under Poisson distribution. The total screening length λ is given by

$$\lambda^{-2} = \lambda_e^{-2} + \lambda_i^{-2}. \quad (2.7)$$

With this screening length the potential about a donor becomes

$$V(r) = [-q^2 \exp(-r/\lambda) / 4\pi\epsilon\epsilon_0 r]. \quad (2.8)$$

To estimate the average lowering of the conduction band edge, we concentrate our attention on the potential between two impurities which are separated by the average distance between donors. The average shift can be divided into two parts. First, the conduction electron barrier height is lowered due to the overlap of the potential of ionized donors as illustrated in Fig. 1. Second, the conduction band edge actually occurs somewhat below the maximum of the potential due to electron tunneling. We first calculate the maximum of the potential. If only the nearest neighbor is considered, the lowering of the barrier height as shown in Fig. 1 is approximately equal to

$$\Delta E_{1c} \cong \frac{2q^2 \exp(-d/2\lambda)}{4\pi\epsilon\epsilon_0 (\frac{1}{2}d)} - \frac{q^2 \exp(-d/\lambda)}{4\pi\epsilon\epsilon_0 d}, \quad (2.9)$$

with $d = (N_D^*)^{-1/3}$, where N_D^* is the ionized donor concentration. The first term in (2.9) corresponds to the potential lowering at the middle point of the two nearby ionized donors. The second term corresponds to the potential lowering at the ionized donor site due to the presence of the nearby ionized donor.

As we have mentioned above, because of electron tunneling the conduction band edge occurs below the maximum in the potential. The location of the average conduction band edge depends upon the shape of the ionized donor potential. We have made a rough estimate about the location of the conduction band edge measured with respect to the maximum in the potential ($-\Delta E_{2c}$), and found that it is small for the cases considered here. Therefore, we can use the result of the rough estimate and it will not introduce significant error in our calculation. The estimate proceeds as follows. We assume that the excited donor state is an extended state if the average radius of the electron wave function of the excited state is half the distance between ionized donors. We also assume that as r becomes large the electron wave function of the excited state approaches

$$\phi_n(\mathbf{r}) \propto \exp(-\alpha r),$$

where $\alpha \equiv (2m^* \Delta E_{2c} / \hbar^2)^{1/2}$ and ($-\Delta E_{2c}$) is the bottom of the conduction band measured with respect to the top of the potential barrier. Hence, the average radius of the electron wave function is approximately equal to α^{-1} . Setting the average radius of the electron wave function to equal to the half distance between ionized donors, i. e., $\alpha^{-1} = \frac{1}{2}d$ we have

$$\Delta E_{2c} = 2\hbar^2 / m^* d^2. \quad (2.10)$$

The total downward shift of the conduction band edge is thus

$$\Delta E_c = \Delta E_{1c} + \Delta E_{2c}. \quad (2.11)$$

For the donor concentrations and temperatures we are interested in, ΔE_c gives significant contribution to the decrease of activation energy, as will be shown in Sec. V.

III. CONDUCTION BAND EDGE TAILING

Donors and acceptors are approximately randomly distributed in the semiconductors. The random distribution of ionized donors and acceptors generates spatial fluctuations in the potential. The potential fluctuation smear out the conduction band edge and thus produce a tail on the conduction-band density of states.⁶

The work of Kane⁶ and Morgan⁷ indicates that the distribution of potential $p(V)$ is approximately Gaussian,

$$p(V) = \frac{1}{(2\pi)^{1/2} \sigma} \exp\left(-\frac{V^2}{2\sigma^2}\right), \quad (3.1)$$

with a standard deviation σ given by

$$\sigma = \left(\frac{N_D^* + N_A}{8\pi^2 \epsilon^2 \epsilon_0^2} q^4 \lambda\right)^{1/2}, \quad (3.2)$$

where λ is the screening length which is given by Eq. (2.7). This distribution of potential fluctuations generates a tail on the conduction-band density of states which extends to minus infinity in energy. However, the mobility of electrons in the density-of-states tail is a function of energy, approaching zero for energies below a certain energy in the tail. For simplicity, we will assume that the mobility is constant for energies greater than $-\sigma$ and that the mobility is zero for energies less than $-\sigma$. Hence, states with energy less than $-\sigma$ do not contribute to the conduction since their mobility is zero.

For slowly varying potential fluctuations, the local density of states at a point with potential V is given by

$$\rho_c(E) = \frac{6\sqrt{2} (m^*)^{3/2}}{\pi^2 \hbar^3} (E - V)^{1/2}. \quad (3.3)$$

The average conduction-band density of states is given by

$$N_c(E) = \int_{-\infty}^E \rho_c(E - V) p(V) dV, \quad E \geq -\sigma \\ = 0, \quad E < -\sigma. \quad (3.4)$$

The magnitude and extent of the conduction-band density of states depends upon the value of σ . For typical values of the parameters, σ can attain values of as large as

10 meV (see discussion in Sec. V). Hence, the broadening of the conduction band edge can lead to significant effects on the observed activation energy.

IV. BROADENING OF DONOR LEVEL

There are two effects which tend to broaden the level. First, the localized wave function of the impurity level at a given impurity has a finite Hamiltonian matrix element with localized wave functions centered at nearby impurities. At finite densities, this leads to broadening of impurity levels into a band of levels. Second, the potential fluctuations due to random distribution of charge impurities lead to changes in the energy of the various localized impurity states.

A. Level broadening due to donor wave-function overlap

For one single isolated shallow donor, such as P, As, or Sb in Si, the hydrogenic model can be applied to define the donor energy state. For semiconductors with shallow donor concentration N_D , the donor ground-state level is discrete but has N_D -fold degeneracy if there is no interaction between the donor impurities. However, if there are finite Hamiltonian matrix elements between the donor ground-state wave functions on different sites, the degeneracy is lifted and the single donor ground energy is broadened into a band. If the overlaps between the donor ground-state wave functions at different sites are small, we can use a tight binding model to estimate the donor level broadening. In this model, the donor level broadening is proportional to the energy transfer integral,¹³

$$J(|\mathbf{R}_i - \mathbf{R}_j|) = \int \frac{q^2}{4\pi\epsilon_0|\mathbf{r} - \mathbf{R}_i|} \phi_0(\mathbf{r} - \mathbf{R}_i)\phi_0(\mathbf{r} - \mathbf{R}_j) d^3\mathbf{r}, \quad (4.1)$$

where $\phi_0(\mathbf{r})$ is the donor ground-state wave function. Using a scaled hydrogenic model for the donor ground-state wave function, we have

$$\phi_0(\mathbf{r} - \mathbf{R}_i) = (\xi^2/\pi)^{1/2} \exp(-\xi|\mathbf{r} - \mathbf{R}_i|) \quad (4.2)$$

with $\xi = (1/a_H)(E_D/E_0)^{1/2}$, where $(-E_D)$ is the donor ionization energy for the low donor concentration case and $E_0 \equiv -q^2/8\pi\epsilon_0 a_H$ is the ground-state energy calculated from effective mass theory.¹⁴ With $\phi_0(\mathbf{r})$ given in Eq. (4.2), the integration in Eq. (4.1) can be carried out and leads to

$$J(R) = \frac{q^2\xi}{4\pi\epsilon_0} (1 + \xi R) \exp(-\xi R), \quad (4.3)$$

where R is the distance between nearest donor neighbors. As shown in Eq. (4.3), the energy transfer integral $J(R)$ depends exponentially on the nearest donor neighbor distance R . Since the donors are randomly distributed in space, the distance R to the nearest donor neighbor and the energy transfer integral $J(R)$ varies from one donor site to the next. If the donors are absolutely randomly distributed in semiconductors, they should follow a Poisson distribution. In a Poisson distribution, the probability that the nearest donor neighbor lies at a distance R in a spherical shell between R and $R + dR$ is given by

$$4\pi N_D \exp(-\frac{4}{3}\pi N_D R^3) R^2 dR.$$

Therefore, the average energy transfer integral between a donor and its nearest donor neighbor is equal to

$$\langle J(R) \rangle = \int J(R) 4\pi N_D R^2 \exp(-\frac{4}{3}\pi N_D R^3) dR. \quad (4.4)$$

In the tight binding model, the total bandwidth B is equal to $2z|\langle J(R) \rangle|$, where z is the number of nearest neighbors. With a Poisson distribution, there is only one nearest neighbor to every donor and, therefore, z is equal to unity. Hence, the total bandwidth B is given by

$$B = 2|\langle J(R) \rangle|. \quad (4.5)$$

The quantity of importance in our calculation is the impurity-band density of states $\rho_0(E)$. In general, this is a very complicated function of energy. However, for purposes here it suffices to take $\rho_0(E)$ to be a constant over the bandwidth B . That is, if we take midband to occur at zero energy, then

$$\rho_0(E) = N_D/B, \quad -\frac{1}{2}B \leq E \leq \frac{1}{2}B \\ = 0, \quad \text{otherwise.} \quad (4.6)$$

We found for example, that for 10^{18} cm^{-3} shallow donors the donor bandwidth is about 30 meV. Thus, this broadening of the impurity energy level is one of the important effects which have to be included when considering the variation of activation energies as a function of impurity concentration and temperature.

B. Level spreading due to potential fluctuation

As we have mentioned in Sec. III, the random distribution of ionized donors and acceptors generates spatial fluctuations in the potential. If the local potential varies slowly over the size of the wave function, an assumption which is true for the cases considered here, then the donor ground states vary along with the potential fluctuations. Therefore, the impurity states are spread in energy.⁷

The donor-level density of states $\rho_i(E)$, which is appropriate to our calculation, should include both the fluctuation-induced broadening and the broadening due to the energy transfer integral. These two effects can be combined by averaging $\rho_0(E)$ given in Eq. (4.6) over the value of the local potential. That is,

$$\rho_i(E) = \int_{-\infty}^{\infty} \rho_0(E - V) p(V) dV, \quad (4.7)$$

where $p(V)$ is given by Eq. (3.1).

V. CALCULATIONS AND COMPARISON WITH EXPERIMENTAL RESULTS

One way to obtain the impurity activation energy in a semiconductor is to study the conduction electron concentration as a function of temperature (Arrhenus plot). Therefore, in this section we are going to use the results of previous sections and calculate the conduction electron concentrations as a function of temperature.

The conduction electron concentration is given by the standard expression

$$n = \int_{-\infty}^{\infty} \frac{N_c(E) dE}{1 + \exp[(E - E_f)/K_B T]}, \quad (5.1)$$

where $N_c(E)$ has been defined in Eq. (3.4) and E_f is the

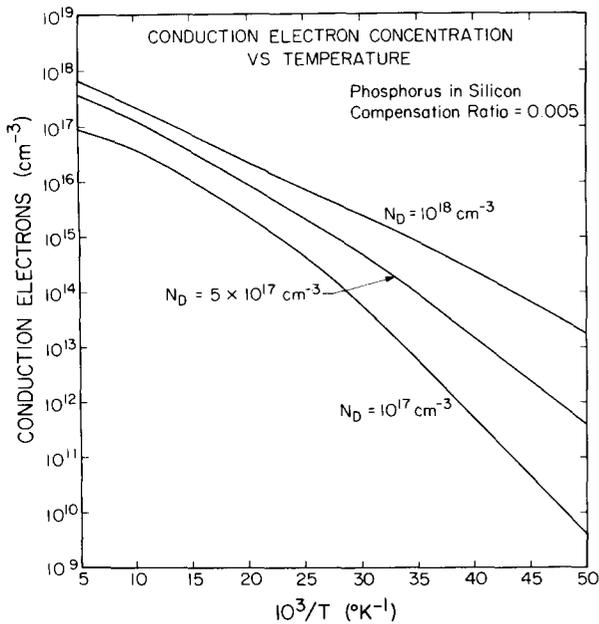


FIG. 2. The conduction electron concentration vs reciprocal temperature for different phosphorus concentrations in silicon. The compensation ratio is 0.5%.

Fermi energy. Similarly, the concentration of ionized donors is defined as

$$N_D^* = \int_{-\infty}^{\infty} \frac{\rho_i(E - E_D') dE}{1 + g \exp[(E_f - E)/K_B T]}, \quad (5.2)$$

where $\rho_i(E)$ is defined in Eq. (4.7) and g is a degeneracy factor; E_D' is the center of the impurity band and is related to the donor ionization energy of a very dilute system ($-E_D$) by

$$E_D' = E_D + \Delta E_c, \quad (5.3)$$

with ΔE_c defined in Eq. (2.11). Charge neutrality leads to

$$n + N_A = N_D^*, \quad (5.4)$$

which determines the Fermi level E_f and, in turn, the electron concentration can be obtained from Eq. (5.1). It should be noted that $\rho_i(E)$ and $N_c(E)$ are functions of σ and σ is a function of n and N_D^* . Hence, n and N_D^* have to be solved self-consistently.

To illustrate these analytical results, we have made numerical calculations of n vs T for shallow donor in

TABLE I. Values for ΔE_c , B , and σ for different donor concentrations and temperatures. The compensation ratio is 0.5%.

N_A and N_D (cm^{-3})	T (°K)	n (cm^{-3})	ΔE_c (meV)	B (meV)	σ (meV)
$N_A = 5 \times 10^{14}$ $N_D = 10^{17}$	25	5.17×10^{11}	1.36	5.58	2.47
$N_A = 2.5 \times 10^{15}$ $N_D = 5 \times 10^{17}$	200	9.06×10^{16}	8.14	5.58	9.59
$N_A = 5 \times 10^{15}$ $N_D = 10^{18}$	25	1.52×10^{13}	1.93	19.3	3.79
$N_A = 2.5 \times 10^{15}$ $N_D = 5 \times 10^{17}$	200	3.73×10^{17}	11.3	19.3	13.6
$N_A = 5 \times 10^{15}$ $N_D = 10^{18}$	25	2.47×10^{14}	2.17	29.8	4.48
$N_A = 2.5 \times 10^{15}$ $N_D = 5 \times 10^{17}$	200	6.59×10^{17}	13.1	29.8	15.7

silicon (for example, P, As, and Sb). The values of ϵ and m^* were taken to 11.8 and $0.33 m_0$, respectively. The degeneracy factor was taken to be 2. In Fig. 2, the calculated n versus the reciprocal of T is plotted for different P concentrations. The compensation ratios K , ratio of acceptors to donors, is fixed at 0.5% and the ionization energy of P in Si at low concentrations is taken to be 44 meV.¹⁵ At this rather small value of compensation ratio the presence of compensation centers is relatively unimportant. The activation energy is proportional to the slope of the Arrhenius plot. We see that as P concentration increases the slope and, hence, the activation energy decreases as expected.

To gauge the relative importance of the various phenomena in this case, we have calculated the values of the ΔE_c , B , and σ at two different temperatures, 200 and 25 °K. These results are given in Table I. From this table, we note that ΔE_c varies by a factor of 4 to 7 between 200 and 25 °K. (This is due to the variation in the number of unoccupied donors and, hence, the potential a free electron in the conduction band sees.) The value of B varies from 5.6 meV at the low concentration of 10^{17} cm^{-3} to 29.8 meV at the high concentration of 10^{18} cm^{-3} . This variation is due to the increase in the energy transfer integral with increasing donor concentrations. The value of σ also shows a considerable variation with temperature and a small variation with donor concentration. The large variation with temperature is due to freeze out of the conduction electrons to the ionized donors.

To investigate the effect of compensation centers on the activation energy, we have calculated conduction electron concentrations vs $1/T$ for fixed P concentration with different compensation ratios. The results for P

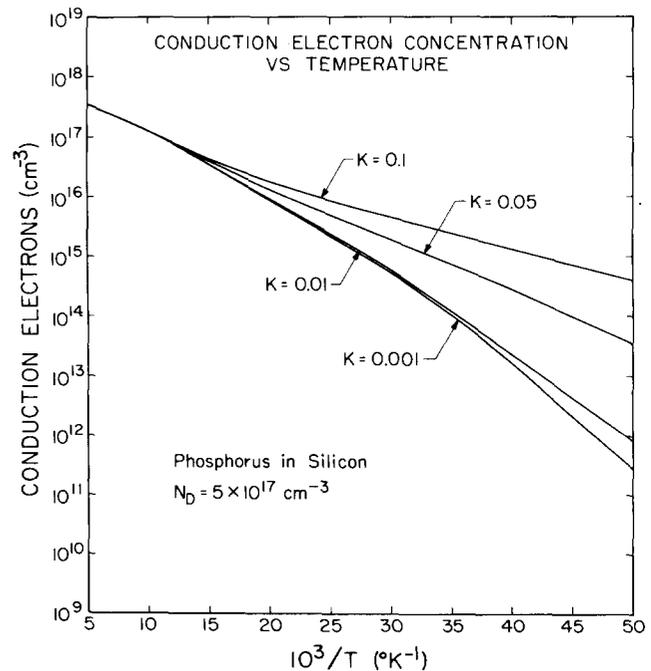


FIG. 3. The conduction electron concentration vs reciprocal temperature for different compensation ratios. The phosphorus concentration is $5 \times 10^{17} \text{ cm}^{-3}$.

TABLE II. Values for ΔE_c , B , and σ for different compensation ratios and temperatures. The donor concentration is $5 \times 10^{17} \text{ cm}^{-3}$.

N_A and N_D (cm^{-3})	K (N_A/N_D)	T ($^{\circ}\text{K}$)	n (cm^{-3})	ΔE_c (meV)	B (meV)	σ (meV)
$N_A = 2.5 \times 10^{15}$ $N_D = 5 \times 10^{17}$	0.5%	25	1.52×10^{13}	1.93	19.3	3.79
$N_A = 5 \times 10^{16}$ $N_D = 5 \times 10^{17}$	10%	200	3.73×10^{17}	11.3	19.3	13.6
$N_A = 5 \times 10^{16}$ $N_D = 5 \times 10^{17}$	10%	25	1.44×10^{15}	5.83	19.3	10.43
$N_A = 5 \times 10^{16}$ $N_D = 5 \times 10^{17}$	10%	200	3.42×10^{17}	12.1	19.3	15.0

concentrations of $5 \times 10^{17} \text{ cm}^{-3}$ are given in Fig. 3. This figure shows that as K increases, the slope and, hence, the activation energy decrease. To show the relative importance of the various phenomena in this case, we have calculated the values of ΔE_c , B , and σ at two different temperatures, 25 and 200 $^{\circ}\text{K}$, and listed the results in Table II. Since ΔE_c is primarily a function of N_D , we note little variation in ΔE_c with changes in K in this range. Again ΔE_c shows a rather large variation with temperature because of the "freeze out" of the conduction electrons. As expected B shows no variation with K since it is a function of the donor concentration only. The values of σ show a small increase with K at fixed T since the magnitude of the fluctuations in the potential increase with increasing compensation. The variation of σ with T is again due to the freeze out of the conduction electrons. As K increases, the conduction band edge lowering ΔE_c and potential fluctuation σ are increased. Therefore, the increase of compensation ratio leads to decrease of activation energy.

These results may be compared with the experimental results of Penin *et al.*¹⁶ and the thorough experimental study of Swartz.¹⁷

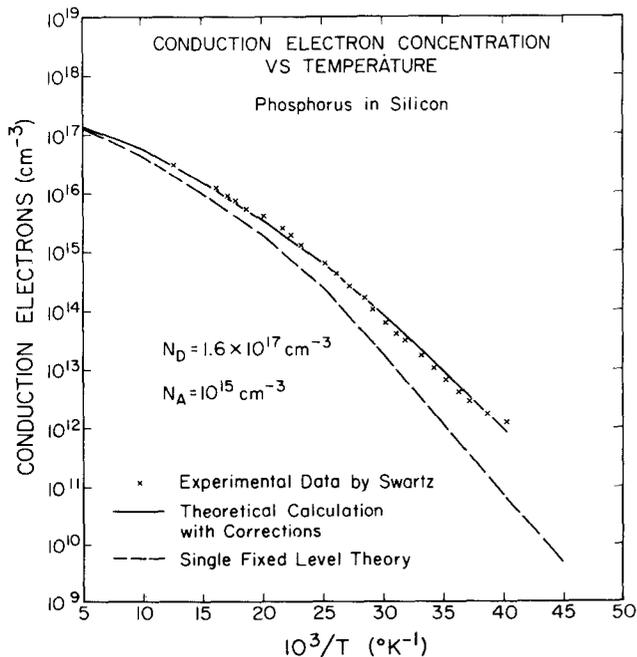


FIG. 4. The experimental and calculated conduction electron concentrations vs reciprocal temperature for phosphorus in silicon. The calculated results for a single fixed level theory is included for comparison.

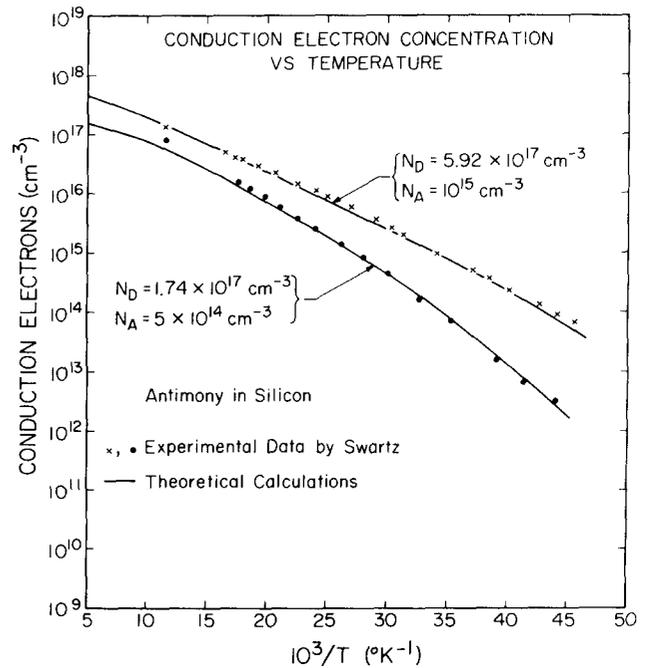


FIG. 5. The experimental and calculated conduction electron concentrations vs reciprocal temperature for antimony in silicon.

The experimental results of Penin *et al.*¹⁶ indicate that the impurity-to-band activation energy depends upon the compensating impurity concentration and decreases as compensating impurity concentrations in Si increase. Thus, the result of our calculation is in qualitative agreement with Penin's experimental result.

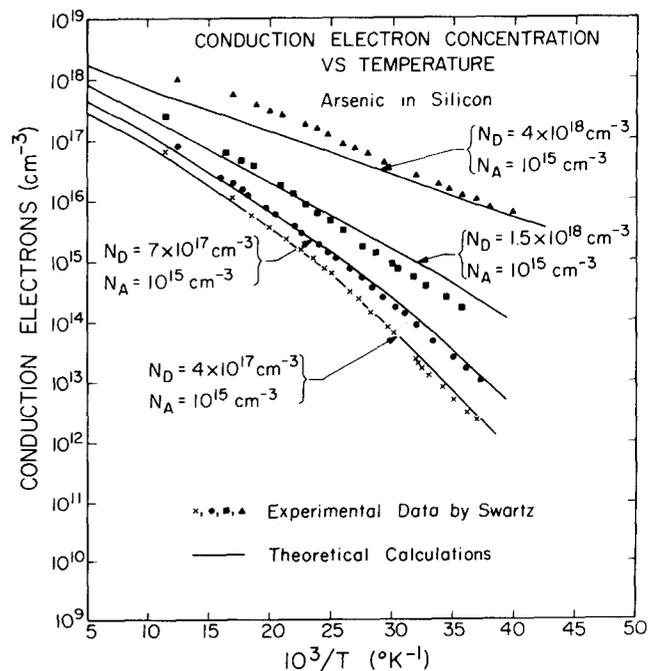


FIG. 6. The experimental and calculated conduction electron concentrations vs reciprocal temperature for arsenic in silicon.

Swartz's¹⁷ results of Hall measurements on Si samples doped with P, As, and Sb provide a rather rigorous check of the theory. Because of a lack of any information about what is the correct value of the Hall coefficient required to convert Hall coefficients to conduction electron concentrations, we take it to be the value appropriate for phonon scattering, $\frac{3}{8}\pi$. The experimental results for conduction electron concentration for P in Si along with calculated electron concentrations are plotted versus $1/T$ in Fig. 4. In this numerical calculation, the donor concentration N_D has been taken to be 1.6×10^{17} P/cm³, a value which produced the best agreement between experiment and theory. The density of compensating centers was determined from the kink in the experimental n -vs- T^{-1} plot to be 10^{15} cm⁻³. As we can see from Fig. 4, the agreement between the theory with all the corrections and experiment is very satisfactory. For comparison, we also plotted in Fig. 4 the calculated conduction electron concentration for a system with fixed activation energy of 44 meV and all the same donor and acceptor concentrations. From Fig. 4 we note that at low temperatures the decrease of activation energy produces a significant increase in the conduction electron concentration.

To compare our calculation with Swartz's experimental results on other dopants, we plotted the calculated electron concentrations vs $1/T$ along with experimental results for Si doped with Sb and As in Figs. 5 and 6, respectively. In these calculations, the ionization energies have been taken to be 39 meV for a very low density of Sb in Si and 49 meV for a very low density of As in Si. In Fig. 5, the compensating acceptor concentrations have been determined in the same way as in the case of P in Si. The Sb concentrations have been chosen to give the best agreement between theory and experiment. As we can see, the agreement is quite good for the case of Sb in Si. In Fig. 6, we compare the experimental and theoretical results for As in Si. The theoretical calculation for the cases $N_D = 4 \times 10^{17}$ cm⁻³ and $N_A = 10^{15}$ cm⁻³, and $N_D = 7 \times 10^{17}$ cm⁻³ and $N_A = 10^{15}$ cm⁻³ are in satisfactory agreement with the experimental results. However, for samples doped with more than 10^{18} As/cm³, we can only obtain qualitative agreement between theory and experiment.

VI. DISCUSSION AND CONCLUSIONS

The self-consistent calculation by Lehman and James⁴ essentially include two effects: the lowering of the conduction band edge and the shift of the ground-state level of the donor due to conduction electron screening. While their results are successful at accounting for experimental results at small donor concentrations and with small amounts of compensation, they are inadequate at higher impurity concentrations. In this paper, we have introduced two additional effects; the broadening of the impurity level due to a finite energy transfer integral between wave functions localized on neighboring sites and potential fluctuations, and the tail on the conduction band edge due to potential fluctuations. The addition of these effects was shown to bring about good agreement between experimental results and theory for moderate impurity concentrations. However, at even higher impurity concentrations ($N_D \geq 4 \times 10^{18}$ cm⁻³), even these

effects are incapable of explaining the experimental results. This suggests that the problem is more complicated in this range.

The importance of broadening of the impurity level and band tailing on the conduction band edge found in these calculations suggest that one may not think of the single activation energy for $N_D \geq 10^{17}$ cm⁻³. Interpretation of the Arrhenus plot in terms of single activation energy would then require a temperature-dependent activation energy.

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APPENDIX

In this Appendix, we calculate the shift of donor ground-state level due to the conduction electron screening. We first calculate the potential due to a donor atom, i. e., one ionized donor plus one trapped electron. In response to the potential of the donor atom, the conduction electrons readjust themselves to screen the potential. We calculate the screening conduction electron distribution by using the linearized Hartree approximation. Since the potential due to the screening conduction electrons is small, we then calculated the donor ground-state level by using first-order perturbation theory.

To obtain the potential due to the donor ion and trapped electron, we assume that the trapped donor electron has a 1s ground-state wave function with Slater coefficient, i. e.,

$$\phi_0(\mathbf{r}) = (\xi^3/\pi) \exp(-\xi r), \quad (\text{A1})$$

where $r = |\mathbf{r}|$. The potential of the neutral donor atom is thus

$$V_n(\mathbf{r}) = \frac{q^2}{4\pi\epsilon_0} \left(\frac{1}{r} + \xi \right) \exp(-2\xi r). \quad (\text{A2})$$

Subject to the neutral donor atom potential $V_n(\mathbf{r})$ the conduction electrons readjust themselves and try to screen the potential. Under the Hartree approximation and linear response theory, the screened potential is given by

$$V_{nc}(\mathbf{r}) = (2\pi)^{-3} \int \tilde{V}_{nc}(\mathbf{K}) \exp(i\mathbf{K} \cdot \mathbf{r}) d^3K, \quad (\text{A3})$$

with

$$\tilde{V}_{nc}(\mathbf{K}) = \frac{\tilde{V}_n(\mathbf{K})}{1 + \tilde{V}_n(\mathbf{K}) \epsilon_0 / q \lambda_e^2}, \quad (\text{A4})$$

where λ_e is the conduction electron screening length and $\tilde{V}_n(\mathbf{K})$ is the Fourier transformation of $V_n(\mathbf{r})$, i. e.,

$$\begin{aligned} \tilde{V}_n(\mathbf{K}) &\equiv \int V_n(\mathbf{r}) \exp(-i\mathbf{K} \cdot \mathbf{r}) d^3r \\ &= \frac{q^2}{\epsilon_0} \left(\frac{K^2 + 8\xi^2}{(K^2 + 4\xi^2)^2} \right), \end{aligned} \quad (\text{A5})$$

with $K = |\mathbf{K}|$. In view of Eqs. (A4) and (A5), the integral can be carried out and, for $\xi \lambda_e > \frac{1}{4}$, leads to

$$V_{nc}(\mathbf{r}) = \frac{2q^2}{\pi\epsilon\epsilon_0 r} \lambda_e^2 \xi^2 f \exp(-2g\xi r) \sin(2 \tan^{-1} f + 2h\xi),$$

with

$$f = (16\xi^2 \lambda_e^2 - 1)^{1/2},$$

$$g = \left[\frac{1}{2} + \frac{1}{16\xi^2 \lambda_e^2} + \left(\frac{1}{2} + \frac{1}{2\xi^2 \lambda_e^2} \right)^{1/2} \right]^{1/2},$$

and

$$h = \left[\frac{1}{2} \left(1 + \frac{1}{2\xi^2 \lambda_e^2} \right)^{1/2} - \frac{1}{2} - \frac{1}{16\xi^2 \lambda_e^2} \right]^{1/2}.$$

For the case we are interested in, the conduction electron screening length is larger than the trapped electron average radius $1/\xi$, i. e., $\lambda_e \xi > 1$. The series expansion of $V_{nc}(\mathbf{r})$ to the first order of $1/\xi\lambda_e$ gives

$$V_{nc}(\mathbf{r}) \cong \frac{q^2 \xi \lambda_e}{2\pi\epsilon\epsilon_0 r} \exp(-2\xi r) \sin\left(\frac{1+\xi r}{2\xi\lambda_e}\right), \quad (\text{A7})$$

with the residual terms of the order of $(1/\xi\lambda_e)^2$. Therefore, the potential due to a donor ion and screening electrons only is given by

$$\begin{aligned} V_c(\mathbf{r}) &= V_{nc}(\mathbf{r}) + \frac{q^2}{4\pi\epsilon\epsilon_0} \left[\frac{1}{r} - \left(\frac{1}{r} + \xi \right) \exp(-2\xi r) \right] \\ &= \frac{q^2}{4\pi\epsilon\epsilon_0 r} - \frac{q^2 \exp(-2\xi r)}{4\pi\epsilon\epsilon_0} \left[\frac{1}{r} + \xi - \frac{2\xi\lambda_e}{r} \sin\left(\frac{1+\xi r}{\lambda_e \xi}\right) \right]. \end{aligned} \quad (\text{A8})$$

The potential seen by the trapped electron is different from the Coulomb potential by

$$V'(\mathbf{r}) = - \frac{q^2 \exp(-2\xi r)}{4\pi\epsilon\epsilon_0} \left[\frac{1}{r} + \xi - \frac{2\xi\lambda_e}{r} \sin\left(\frac{1+\xi r}{2\xi\lambda_e}\right) \right], \quad (\text{A9})$$

and the ground-state energy shift in first-order perturbation theory is given by

$$\begin{aligned} \Delta E_B &= V'_{00} \equiv \langle \phi_0 | V' | \phi_0 \rangle \\ &= \frac{q^2 \xi}{4\pi\epsilon\epsilon_0} \left(\frac{3}{8} - \frac{2\xi\lambda_e \sin[(1/2\xi\lambda_e) + 2 \tan^{-1}(1/8\xi\lambda_e)]}{4 + 1/16\xi^2 \lambda_e^2} \right). \end{aligned} \quad (\text{A10})$$

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†Present address: Hewlett-Packard Laboratories, Palo Alto, Calif. 94304.

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