

The amplitude, A , of $eq(R_{ik})$ has dropped out in terms of n_0^2 . This is the virtue of considering the quantity $\alpha^2 n_0$. To go further and obtain an approximate value, $\cos^2(2k_F R_i + \varphi)$ is taken to be $\frac{1}{2}$. Further, the sum over i converges rapidly and there is little error in summing over all shells when $n_0=98$, the value found by Row-

land¹⁷ for zinc in aluminum. Since $\sum_i (r_0/R_i)^6 \cong 115$ for a face-centered cubic lattice, therefore,

$$\alpha^2 n_0 \cong (98/18)^2 \times 115 \cong 3500.$$

This value of $\alpha^2 n_0$ is compared in Part IV with the value deduced from experiment.

Effect of Pressure on the Energy Levels of Impurities in Semiconductors. I. Arsenic, Indium, and Aluminum in Silicon*

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The changes in resistivity of silicon samples containing group III and group V impurities have been measured at hydrostatic pressures up to 6000 kg cm⁻² at 50°K. The changes are explained by a dependence on pressure of the ionization energy of the majority impurity center. The results indicate that the arsenic energy level moves toward the conduction-band edge at a rate of approximately 5×10^{-8} eV kg⁻¹ cm². The energy levels for indium and aluminum move away from the valence-band edge at rates of about 5×10^{-8} eV kg⁻¹ cm² and 1×10^{-8} eV kg⁻¹ cm², respectively. Corrections for the changes in mobility with pressure have been applied for the n -type sample. The motion of the arsenic energy level is explained by a change in dielectric constant and effective mass with pressure, and indicates a change in the average effective mass of less than 1% in 5000 kg cm⁻². The very small changes in ionization energy, while expected, are to be contrasted with the much larger changes found for the deep-lying levels produced by elements such as gold.

INTRODUCTION

THE effects of high hydrostatic pressure on the properties of a number of semiconductors can be understood using a model based on changes in the band structure of the materials.¹ For germanium and silicon, the pressure variation of the intrinsic resistivity,² the carrier mobilities,³ the magnetoresistance coefficients,⁴ the fundamental absorption edge,⁵ and the dielectric constant⁶ can be explained by the shift of the appropriate band edges with pressure. Since some of the most important properties of semiconductors are due to the presence of foreign atoms in the host lattice, the effect of pressure on the ionization energy of the electrons or holes on certain of these impurity

centers has been measured, with the hope that the present model can be used to explain the results.

The best understood impurity atoms in germanium and silicon are the so-called "hydrogenic" impurities, the group III and group V elements of the periodic table. The simple theory⁷ predicts that the impurity ionization energy will be given by

$$E = (e^2 m_{\text{eff}}) / (2a_h m_0 K^2), \quad (1)$$

where m_{eff} is the electron effective mass, m_0 the electron mass, K the dielectric constant, e the electronic charge, a_h the radius of the first Bohr orbit in hydrogen, and $e^2/2a_h = 13.62$ eV = the ionization energy of hydrogen. The quantum-mechanical treatment of Kohn and Luttinger⁸ also gives Eq. (1) for n -type silicon. For p -type silicon the approximations leading to Eq. (1) do not hold. Experimentally, the ionization energy can be related to the number of current carriers in the crystal. In general, the relation between the carrier density n and the impurity ionization energy E can be quite complex, but at low enough temperature we can write⁹

$$n = A \exp(-E/kT), \quad (2)$$

⁷ H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 102.

⁸ See W. Kohn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 280.

⁹ See reference 7, p. 124.

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¹ W. Paul, *J. Phys. Chem. Solids*, **8**, 196 (1959) (and references quoted therein).

² W. Paul and H. Brooks, *Phys. Rev.* **94**, 1128 (1954); W. Paul and G. L. Pearson, *ibid.* **98**, 1755 (1955).

³ A. C. Smith, *Bull. Am. Phys. Soc.* **3**, 14 (1958); A. C. Smith, Technical Report H. P. 2, Gordon McKay Laboratory, Harvard University, 1958 (unpublished).

⁴ G. B. Benedek, W. Paul, and H. Brooks, *Phys. Rev.* **100**, 1129 (1955).

⁵ W. Paul and D. M. Warschauer, *J. Phys. Chem. Solids* **5**, 89, 102 (1958); **6**, 6 (1958).

⁶ M. Cardona, W. Paul, and H. Brooks, *J. Phys. Chem. Solids*, **8**, 204 (1959).

where A is a constant which depends on the densities of donors and acceptors, the effective mass and the temperature. The maximum temperature for which Eq. (2) holds is about 15°K for germanium and about 55°K for silicon.¹⁰ An investigation of the freezing curve of helium as a function of temperature shows that helium freezes at about 1500 kg cm^{-2} at 15°K and about 7000 kg cm^{-2} at 55°K .¹¹ Thus, the larger pressure range, and the greater ease of obtaining the temperature, has made the investigation of hydrogenic levels more feasible in silicon than in germanium.

In these experiments the change in resistivity with pressure at low temperatures is measured and the results analyzed—using estimated mobility and effective mass changes—to give the dependence of impurity ionization energy on pressure.

APPARATUS AND METHOD

These experiments were carried out using Bridgman's gas apparatus,¹² suitably modified so that the temperature of the sample container could be well controlled. This apparatus uses commercially available gases such as helium as pressure transmitting fluids and can be used to obtain a maximum pressure of 7500 kg cm^{-2} at temperatures above 77°K ; this limit is set by the mechanical strength of the apparatus. At lower temperatures the maximum pressure is determined by the pressure at which helium freezes; for example, 7000 kg cm^{-2} at 50°K .

In the Bridgman apparatus, the experimental vessel was connected to the main cylinder by a steel connecting pipe about 18 in. long. Electrical leads from the sample were carried up through this pipe and out of the apparatus at plugs in the main cylinder at room temperature. This arrangement is inadequate in measurements requiring a high degree of temperature control because of the considerable heat leak down the pipe to the sample bomb.

To improve the temperature control of the sample bomb, stainless steel pressure tubing¹³ was used between the pressure-generating system and a new, larger sample bomb. Since the whole length of stainless steel tubing can be put into a temperature bath, the heat leak to the bomb is reduced to a negligible amount. Fortunately, the tubing can be sealed into the system in the conventional way.¹³ The solder joints seal gas at all temperatures investigated.

The length of stainless tubing used made it impossible to use Bridgman's electrical terminals. The leads were brought directly out of a plug in the sample container.

¹⁰ F. J. Morin and J. P. Maita, *Phys. Rev.* **96**, 28 (1954); P. Debye and E. M. Conwell, *Phys. Rev.* **93**, 693 (1954).

¹¹ J. S. Dugdale and F. E. Simon, *Proc. Roy. Soc. (London)* **A218**, 291 (1953).

¹² P. W. Bridgman, *Proc. Am. Acad. Arts and Sci.* **67**, 305 (1932).

¹³ W. Paul and D. M. Warschauer, *Rev. Sci. Instr.* **27**, 418 (1950), M. G. Holland, Technical Report, H. P. 4, Gordon McKay Laboratory, Harvard University, 1958 (unpublished).

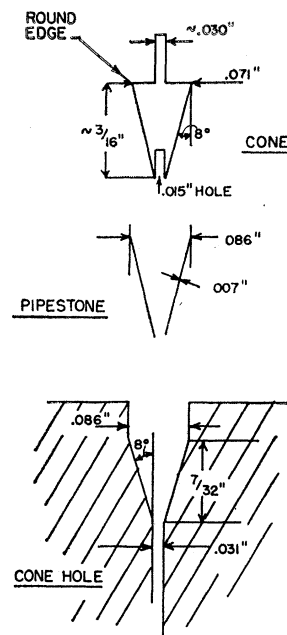


FIG. 1. Details of electrical lead-in to pressure vessel.

Special terminals were necessary since they must operate at 50°K . The conventional drill rod cone and pipestone insulator which works well with liquid will seldom seal gas even at room temperature. The cone is better made to match the plug in which it is to be sealed, both in steel type and hardness. The plug and cones were made of Omega tool steel hardened to Rockwell C 35. The cones and coned holes must be very carefully made and scratch-free. The 0.007-in. pipestone insulator is soaked in very thick silicone oil,¹⁴ (Dow Corning DC 200, 12 500 centistokes) before assembly, and mixed pipestone powder and oil put on top of the cone; the oil must be replaced on top of the cones about every third pressure run. The details of one of these insulators are shown in Fig. 1.

The cryostat used is shown in Fig. 2. It is a conventional double Dewar system in which the desired temperature (about 50°K) is obtained by reducing the vapor pressure above the liquid nitrogen (above 63°K) or solid nitrogen in the inner Dewar. The Dewars are both of stainless steel, the outer one 6 in. inside diameter and 3 ft deep, the inner one $4\frac{1}{2}$ in. inside diameter and 2 ft deep. A brass plate is sealed to the inner Dewar with a rubber O-ring and has the stainless steel pressure tubing sealed in with a lead seal. The rubber O-ring is below the nitrogen level in the outer Dewar, and, although very stiff, still can hold a vacuum of the order of 5×10^{-4} mm Hg.

The manostat, which operates on the principle of the Cartesian diver¹⁵ is used to control the vapor

¹⁴ We are indebted to Professor F. Birch for advising the use of silicone oil.

¹⁵ R. Gilmont, *Anal. Chem.* **23**, 157 (1951); R. Gilmont, *Anal. Ed. Ind. Eng. Chem.* **18**, 633 (1946).

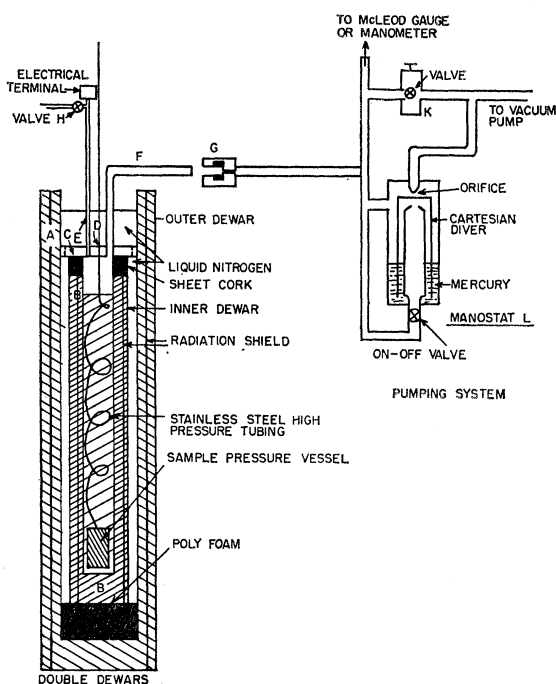


FIG. 2. Schematic drawing of the double Dewar temperature control system used with the pressure vessel. *A* is outer Dewar; *B* is inner Dewar; *C* is a brass sealing plate; *D* is a lead seal for the pressure tubing; *E* is an exit for electrical leads; *F* is a filling tube; *G* is a vacuum connector; *H* is an escape valve; *K* is a bypass valve; *L* is a manostat.

pressure above the nitrogen and thus to regulate the temperature of the pressure vessel. The sensitivity of the manostat gives a maximum temperature variation of 0.01°K at 1 mm vapor pressure. However, the method to be described below affords a means of obtaining an effective temperature control better by a factor of 5. The temperature is measured in two ways. First, a calibrated copper-constantan thermocouple is used to measure the absolute temperature to $\pm 1\%$. Second, the change in resistance of an appropriate silicon or germanium sample is used to indicate the changes in temperature to less than 0.01°K .

The temperature measurements are made on the outer surface of the bomb but the change in temperature inside and outside the bomb can be correlated very closely, since the temperature variation on the outside is usually less than 0.1°K , in several hours. Two nearly identical samples are used, the first the experimental sample inside the pressure vessel, the second attached to a copper block in good thermal contact with the bomb and electrically in series with the experimental sample. Instead of trying to obtain a constant temperature, we adjust the manostat so that the vapor pressure and the temperature increase very slowly. After a change of about 0.05 to 0.1°K , the manostat is adjusted so that the vapor pressure and the temperature decrease slowly. If $\log_{10}R_p$ is plotted vs $\log_{10}R_c$ (R_p is the resistance of the sample in the bomb and R_c is the resistance

of the comparison sample), as the temperature changes, a straight line is obtained. Figure 3 shows a typical curve for increasing and decreasing temperature; the difference in the increasing and decreasing temperature curves is one measure of the error in the method.

If the pressure is changed during the temperature cycle, there is an initial change in the temperature inside the bomb, and then a return to equilibrium, usually after a few minutes, although in some experiments it was as much as $\frac{3}{4}$ of an hour. This is shown in Fig. 4 by the initial deviation from the straight line. The reproducibility is also seen in Fig. 4. As the pressure is increased and then decreased to the initial value, the extrapolated curves are seen to overlap. It is also of interest that an increase of pressure, which is accompanied by a temperature increase inside the bomb, causes an increase in temperature on the outer surface of the bomb. This indicates the sensitivity of the method.

A fixed relationship between the temperatures of the two samples is required, and not necessarily temperature equality. The method gives a pressure coefficient for the resistance of the sample even when this resistance change is so small that it would normally be hidden by temperature fluctuations of less than 0.05°K . The method breaks down and the sample temperatures do not follow each other if the temperature variation is too fast or too uneven, as, for example, in coolant baths such as liquid oxygen or liquid nitrogen at atmospheric pressure. In this manner an effective temperature control of $\pm 0.002^\circ\text{K}$ can be obtained. The absolute temperature need only be known accurately to 1% or $\pm 0.5^\circ$ at 50°K .

After the silicon samples had been chemically nickel plated,¹⁶ Teflon-covered wires were soldered on using

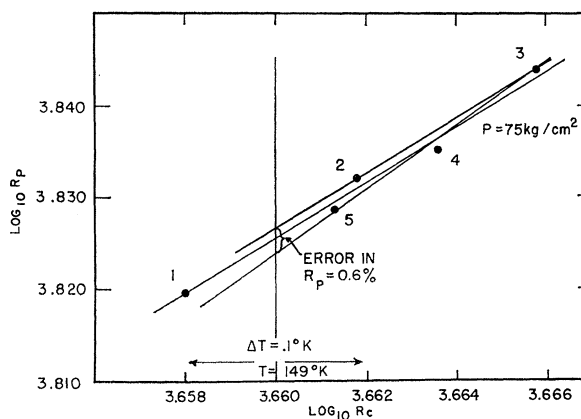


FIG. 3. Illustration of the method of obtaining sample resistances as a function of pressure at a fixed temperature. This figure shows the relation between the temperature inside and the temperature outside of the vessel. These illustrative data were taken using gold-doped germanium resistors near 150°K . Points 1-5 were taken in succession while first decreasing, then increasing, the temperature.

¹⁶ A. Brenner, *Metal Finishing* **52**, 68 (November, 1954); **52**, 61 (December, 1954).

Cerroseal-35 solder.¹⁷ These contacts were found to be mechanically strong and Ohmic.

The resistivity was obtained using a four-probe method. The potential drop across a standard resistance (for current measurement) and across the sample voltage probes was measured with a potentiometer and high-sensitivity galvanometer. The accuracy of the measurement is of the order of 0.01%. Since we are interested only in the ratio of resistivity at pressure P to that at zero pressure, the dimensions of the sample are unimportant as long as there is negligible change with pressure. In 6000 kg cm^{-2} this amounts to a correction of about 0.2% in $\rho(6000)/\rho(0)$, which is much less than the error in the measurement of $R(6000)/R(0)$.

The pressure is measured using a manganin wire gauge calibrated against an assumed freezing pressure of Hg at 0°C of 7640 kg cm^{-2} ¹⁸ and is accurate to about 1%. The sample resistance could not be measured every 1000 kg cm^{-2} or so as is the normal procedure since the experimental method required lengthy measurement at any one pressure. The capacity of the Dewar for solid nitrogen permitted only three pressure points for each sample, but each of these points was determined three or four times during the pressure and temperature cycling employed. (See Fig. 4.)

THEORY

It is a straightforward matter to obtain the formula of DeBoer and van Geel concerning the carrier statistics.¹⁹

$$\frac{n(N_a+n)}{N_d-N_a-n} = \frac{A_n}{g_n} \exp[(E_d-E_c)/kT] = \frac{\Phi_n}{g_n}, \quad (3)$$

$$\frac{p(N_a+p)}{N_a-N_d-p} = \frac{A_p}{g_p} \exp[(E_v-E_a)/kT] = \frac{\Phi_p}{g_p}.$$

Here, n =number of electrons in the conduction band, p =number of holes in the valence band, N_d =number of donor impurities, N_a =number of acceptor impurities, E_c-E_d is the ionization energy of the ground state of the donor electron, E_a-E_v is the same for an acceptor hole, the g 's are ground state degeneracies (the excited states can be neglected at 50°K),²⁰ and A_n and A_p are the density-of-state factors for the conduction and valence bands, respectively.

Also,

$$A_n = 2(2\pi m_0/h^2)^{3/2} (kT)^{3/2} (m_l m_t^2/m^3)^{1/2},$$

$$= 2.436 \times 10^{19} (T/294)^{3/2} (m_{\text{eff}n}/m_0)^{3/2},$$

$$A_p = 2.436 \times 10^{19} (T/294)^{3/2} (m_{\text{eff}p}/m_0)^{3/2},$$

$$m_{\text{eff}p} = [m_{1p}^{3/2} + m_{2p}^{3/2}]^{2/3},$$

¹⁷ Made by Cerro De Pasco Corporation, New York, New York.

¹⁸ P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1949), p. 72; see also D. M. Warschauer and W. Paul, *Rev. Sci. Inst.* **29**, 675 (1958).

¹⁹ J. H. DeBoer and W. C. van Geel, *Physica* **2**, 186 (1935).

²⁰ C. A. Klein (private communication).

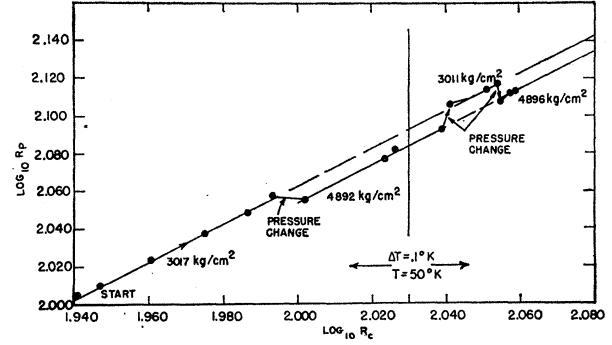


FIG. 4. Illustration of the method of obtaining sample resistances as a function of pressure at a fixed temperature. The temperature is allowed to vary slowly within close limits while being monitored through the resistance of a temperature-sensitive sample mounted *outside* of the pressure vessel. A fixed value of the comparison resistance *outside* is taken to correspond to a fixed temperature *inside* the pressure vessel.

where m_l and m_t are the longitudinal and transverse effective masses in the conduction band, and the constant energy surfaces are ellipsoids of revolution; $m_{\text{eff}n}$ is the density-of-states effective mass for the conduction band; $m_{\text{eff}p}$ is a similarly defined density-of-states effective mass for the degenerate valence band and is an average over the curvatures in two degenerate valence bands; and m_{1p} and m_{2p} are the heavy- and light-hole masses in the valence band.

At room temperature the number of carriers is temperature independent and is given by

$$n = N_d - N_a,$$

$$p = N_a - N_d,$$

At very low temperature, where n is much less than N_a and $N_d - N_a$, the number of carriers becomes

$$n = [(N_d - N_a)/N_a] \Phi_n / g_n. \quad (4a)$$

With similar approximations,

$$p = [(N_a - N_d)/N_d] \Phi_p / g_p. \quad (4b)$$

It will not be necessary to discuss analytic solutions and corrections other than Eq. (4) since the samples all obeyed these equations at the temperatures of measurement.

Once we have the equations relating the number of carriers to the ionization energy, the resistivity equation is used to relate it to an experimentally measurable quantity.

$$\rho = (ne\mu_n + pe\mu_p)^{-1}, \quad (5)$$

where ρ =resistivity in $\Omega\text{-cm}$, e =electronic charge= 1.6×10^{-19} C, μ_n =electron mobility in $\text{cm}^2/\text{V-sec}$, and μ_p =hole mobility in $\text{cm}^2/\text{V-sec}$. If

$$(E_c - E_d) = (E_c - E_d)_{P=1} + \alpha_n P,$$

where

$$\alpha_n = \left(\frac{\partial (E_c - E_d)}{\partial P} \right)_T, \quad (6)$$

henceforth written dE/dP , and P is the pressure in kg cm^{-2} , then at low temperatures

$$\frac{d \ln \rho_n}{dP} = \frac{\alpha_n}{kT} \left\{ \frac{d \ln \mu_n}{dP} + \frac{d \ln A_n}{dP} \right\}$$

and

$$\frac{d \ln \rho_p}{dP} = \frac{\alpha_p}{kT} \left\{ \frac{d \ln \mu_p}{dP} + \frac{d \ln A_p}{dP} \right\}. \quad (7)$$

The mobilities are determined by a relaxation time which is the result of scattering both by lattice vibrations and ionized impurities. While, strictly speaking,²¹ the mobility is given by an average over a Fermi-Dirac distribution of a relaxation time $\tau(\epsilon)$, where

$$1/\tau_n(\epsilon) = 1/\tau_L(\epsilon) + 1/\tau_I(\epsilon),$$

to a first approximation we can write

$$1/\mu_n = 1/\mu_{Ln} + 1/\mu_{In} \quad (8)$$

where τ_n , μ_n = total relaxation time and mobility, $\tau_L(\epsilon)$, μ_{Ln} apply to lattice scattering and $\tau_I(\epsilon)$, μ_{In} to impurity scattering of electrons.

Equation (8) will be used for n -type material. For p -type material there are two valence bands (neglecting the band split off by spin-orbit coupling) called the high- and low-mass bands, and the mobility and number of carriers used in Eq. (5) must be defined as follows²¹:

$$\begin{aligned} p &= p_1 + p_2, \\ \mu_p &= (p_1 \mu_1 + p_2 \mu_2) / (p_1 + p_2), \\ 1/\mu_i &= 1/\mu_{Li} + 1/\mu_{Ii} \quad i = 1, 2, \end{aligned} \quad (9)$$

where the subscript 1 applies to the heavy hole band, the subscript 2 to the light hole band, L to lattice scattering and I to ionized impurity scattering. The values of p_i are still obtained from Eq. (4) by replacing Φ_p by

$$\Phi_i = (A_i/g_p) \exp[(E_v - E_a)/kT], \quad \Phi_1 + \Phi_2 = \Phi_p,$$

where

$$A_i = 2.436 \times 10^{19} (T/294)^{3/2} (m_i/m_0)^{3/2}$$

and

$$A_1 + A_2 = A_p.$$

Using Eq. (8), we can obtain for n -type material

$$\begin{aligned} \alpha_n = \frac{dE}{dP} = kT \left\{ \frac{d \ln \rho_n}{dP} + \frac{d \ln A_n}{dP} \right. \\ \left. + \frac{\mu_n}{\mu_{Ln}} \frac{d \ln \mu_{Ln}}{dP} + \frac{\mu_n}{\mu_{In}} \frac{d \ln \mu_{In}}{dP} \right\}. \quad (10) \end{aligned}$$

For the donor level, using Eq. (1) we have

$$\frac{d \ln E}{dP} = \frac{d \ln m_{\text{eff}}}{dP} - 2 \frac{d \ln K}{dP}. \quad (11)$$

²¹ F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 199; see also reference 7, p. 158.

For p -type material the pressure effect is found from

$$\begin{aligned} \alpha_p = \frac{dE}{dP} = kT \left\{ \frac{d \ln \rho_p}{dP} + \frac{1}{p_1 \mu_1 + p_2 \mu_2} \left[p_1 \mu_1 \frac{d \ln A_1}{dP} \right. \right. \\ \left. \left. + p_2 \mu_2 \frac{d \ln A_2}{dP} + p_1 \mu_1 \frac{d \ln \mu_1}{dP} + p_2 \mu_2 \frac{d \ln \mu_2}{dP} \right] \right\}, \quad (12) \end{aligned}$$

$$\frac{d \ln \mu_i}{dP} = \frac{\mu_i}{\mu_{Li}} \frac{d \ln \mu_{Li}}{dP} + \frac{\mu_i}{\mu_{Ii}} \frac{d \ln \mu_{Ii}}{dP}, \quad i = 1, 2.$$

In order to discuss the temperature dependence of the ionization energy we must define more precisely which energy enters Eqs. (2) to (12). The term $E_c - E_d$ (or $E_v - E_a$) is a free energy, and precisely, a partial Gibbs free energy.²² The slope at low temperatures of a graph of \ln (resistivity) vs reciprocal temperature gives the 0°K energy difference²³; any linear temperature dependence in $(E_c - E_d)$ will not change the slope. The implicit temperature dependence is found from

$$\left(\frac{\partial E}{\partial T} \right)_P = \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial E}{\partial P} \right)_T = -\alpha_n (\beta/\kappa), \quad (13)$$

where

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \text{thermal expansion coefficient},$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \text{compressibility}.$$

The explicit temperature dependence of the ionization energy has not as yet been determined, although for the forbidden gap in silicon and germanium, this explicit dependence is larger than the implicit volume dependence.²

However, in the pressure measurements one measures the pressure coefficient of energy at the temperature of the measurement. This will equal the pressure coefficient of the 0°K ionization energy only if the pressure dependence of the temperature coefficient of the ionization energy is negligible.

For n -type silicon, the pressure coefficient of the ionization energy can be simply interpreted in terms of changes in effective mass and dielectric constant. The theory for the ionization energy of shallow acceptors is more complicated,^{3,24} so that no simple description of the meaning of changes in the pressure coefficient can be given.

SAMPLE PROPERTIES

Table I lists the properties of the samples studied, which were determined as follows. The value of

²² See reference 7, p. 118.

²³ See reference 7, p. 122; see also H. H. Woodbury and W. W. Tyler, *Phys. Rev.* **105**, 84 (1957).

²⁴ R. G. Shulman, *J. Phys. Chem. Solids* **2**, 115 (1957).

TABLE I. Sample properties. The double entries for μ , μ_I , μ_L in the cases of aluminum and indium impurities refer to the light and heavy holes, respectively.

Impurity	Arsenic	Aluminum	Indium
Ionization energy (eV)	0.049	0.057	0.16
Type	n	p	p
Resistivity (Ω -cm)	1.47 (299°K) 6.11 (50.0°K)	0.549 (297°K) 519 (49.5°K)	0.54 (296°K) 1.18×10^3 (90°K)
Temperature of measurement (°K)	50	49.5	90
μ_I ($\text{cm}^2/\text{V-sec}$)	5.1×10^4	2.3×10^3 4.4×10^3	1.3×10^3 3.1×10^3
μ_L ($\text{cm}^2/\text{V-sec}$)	1.5×10^5	2.4×10^4 7.8×10^4	6.0×10^3 2.0×10^4
μ ($\text{cm}^2/\text{V-cm}$)	3.8×10^4	2.1×10^3 4.2×10^3	1.1×10^3 2.7×10^3
n_0 or p_0 (cm^{-3})	$\sim 3 \times 10^{13}$	$\sim 5 \times 10^{12}$	$\sim 5 \times 10^{12}$
$ N_D - N_A $ (cm^{-3})	2.9×10^{15}	2.1×10^{16}	3.1×10^{16}
No. of majority impurities (cm^{-3})	$\sim 7 \times 10^{15}$	$\sim 3 \times 10^{16}$	7×10^{16}
No. of minority impurities (cm^{-3})	$\sim 4 \times 10^{15}$	$\sim 1 \times 10^{16}$	4×10^{16}

$|N_A - N_D|$ was obtained from the measured room temperature resistivity and the accepted value of the drift mobility.¹⁰ These samples have moderately high doping levels so that the accepted room temperature mobilities may be incorrect due to some contributions from ionized impurity scattering. The value of the minority impurity content was estimated from the resistivity of the starting material, before impurities were added, and can be in error by a factor of 2.

The lattice scattering mobility was calculated using Morin and Maita's formula¹⁰ and the ionized impurity scattering mobility with the Brooks-Herring formula.²⁵ The mass used in the Brooks-Herring formula is the density of states mass, although for n -type silicon this may not be quite correct. Blatt²¹ uses this value and Long and Myers²⁵ find that a mass of $0.3 m_0$ gives a good fit to their mobility data as long as the "ion scattering is not too strong." Brooks²⁶ and Long and Myers²⁵ indicate that the mass may be a complex average of terms of the form $m_i^{1/2}/m_i$. The mobilities are calculated at the temperature of measurement. There may be as much as a factor of 2 error in the values calculated in this way.

n_0 , the number of charge carriers at the temperature of measurement, was deduced from the calculated mobility, and the measured resistivity. There is a possible factor of 2 error in this calculation. Nevertheless, it is clear that $n_0 \ll |N_A - N_D|$ so that the assumptions leading to Eq. (4) are correct.

For the p -type material, the values of μ_{Ii} were found from the Brooks-Herring formula using $m_1 = 0.52 m_0$ and $m_2 = 0.16 m_0$. The values of μ_{Li} were found using the Morin and Maita formula, Eq. (11) and the relations $p_1/p_2 = (m_1/m_2)^{3/2}$, $(\mu_{L1}/\mu_{L2}) = m_2/m_1$. Again, the calculated mobility can be in error by a factor of 2. The value of p_0 was found from the resistivity at the temperature of measurement, Eqs. (5) and (10) and the calculated mobilities. Even if p_0 is in error by a factor of 50, $p_0 \ll |N_A - N_D|$ and the assumptions leading to Eq. (4) are again satisfied.

²⁵ D. Long and J. Myers, Phys. Rev. **115**, 1107 (1959).

²⁶ See reference 7, p. 156.

The apparently large errors in many of these quantities do not seriously affect the deductions from experiment. In each case, it is clear that the condition n_0 (or p_0) $\ll |N_A - N_D|$ holds so that an expression of the form of Eq. (2) holds. The number of both majority and minority impurities only enters the calculation through the ionized impurity mobility. In most cases it is the rate of change of the mobility, not the absolute value, that is important. In the n -type sample it will be seen that the mobility contributes at most 10% to the errors in the calculation. For the p -type samples, the remaining assumptions required in analyzing the data can lead to much larger errors than those due to errors in the mobility.

RESULTS AND INTERPRETATION; DONOR LEVELS

The study of arsenic impurities in silicon by resistivity and Hall coefficient measurements as a function of

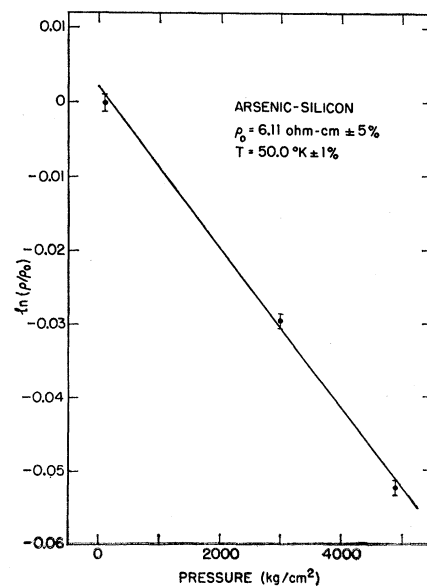


FIG. 5. Resistivity vs pressure for an arsenic-doped silicon sample.

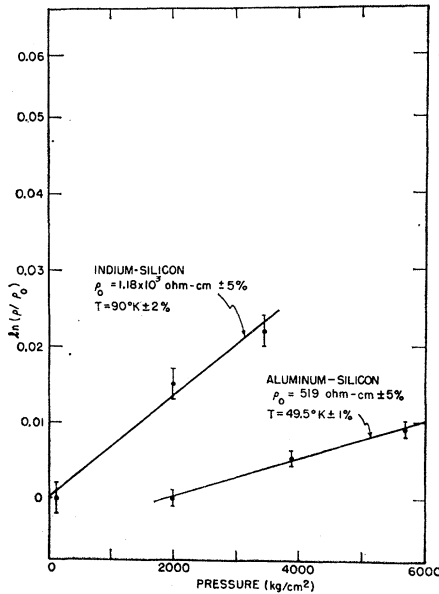


FIG. 6. Resistivity vs pressure for aluminum-doped silicon and indium-doped silicon samples.

temperature shows that the arsenic is de-ionizing below 60°K.¹⁰ Morin and Maita find an activation energy of 0.049 eV in agreement with deductions from the measurement of resistivity vs reciprocal temperature in this laboratory.

Figure 5 is a curve of $\ln(\rho/\rho_0)$ vs pressure for an arsenic-doped silicon sample at 50.0°K. The change in resistivity in 5000 kg cm⁻² corresponds to a temperature change of $\sim 0.2^\circ\text{K}$ at atmospheric pressure. The errors on each point are equivalent to a temperature fluctuation of $\pm 0.002^\circ\text{K}$. From this curve

$$\frac{d \ln \rho}{dP} = -10.9 \times 10^{-6} / \text{kg cm}^{-2} \\ \pm 3\% \text{ up to } 5000 \text{ kg cm}^{-2}.$$

The change in lattice scattering mobility is obtained from the change of sample resistivity with pressure at room temperature. At this temperature the total number of carriers is independent of pressure and the scattering is entirely due to lattice vibrations. The result is

$$\frac{d \ln \mu_n}{dP} = (3.1 \pm 0.1) \times 10^{-6} / \text{kg cm}^{-2} \\ \text{up to } 10\,000 \text{ kg cm}^{-2}.$$

in agreement with measurements by Smith.³ Smith³ also found that for *p*-type germanium the pressure coefficient of the lattice scattering mobility does not change between 200 and 300°K. Paul and Brooks² and Nathan²⁷ have shown, for *n*-type germanium, that the pressure coefficient of the lattice scattering mobility is not temperature-dependent as long as there are no interband scattering effects. Thus, we argue that the

²⁷ M. I. Nathan, Technical Report H. P. 1, Gordon McKay Laboratory, Harvard University, 1958 (unpublished).

pressure coefficient of the lattice scattering mobility for silicon does not change with temperature between room temperature and 50°K. This is quite plausible when one realizes that the pressure coefficient of the lattice scattering is due to the change in effective mass and elastic constants. The temperature coefficient of the pressure coefficient will certainly be a higher-order effect.

A_n depends on the pressure through the effective mass and μ_{In} through the effective mass and the dielectric constant. Since it will be shown that the change in effective mass with pressure is small, the change in A_n and μ_{In} with pressure due to a change in effective mass will be neglected to a first approximation. The change of the dielectric constant with pressure has been found by Cardona, Paul, and Brooks⁶ to be

$$\frac{d \ln K}{dP} = -(0.4 \pm 0.1) \times 10^{-6} / \text{kg cm}^{-2}.$$

This is included in the change in μ_{In} with pressure.

Thus, as a first approximation we obtain, using Eq. (10),

$$\frac{dE}{dP} = -4.6 \times 10^{-8} \pm 4\% \text{ eV kg}^{-1} \text{ cm}^2$$

and from Eq. 11

$$\frac{d \ln m_{\text{eff}}}{dP} = -(1.7 \pm 0.2) \times 10^{-6} / \text{kg cm}^{-2}.$$

The errors here are just those due to the measurements.

The m_{eff} which we have calculated is approximately the geometric average⁸ ($m_l m_t$)^{1/2}. Thus, we can say it is the same mass found in the term, A_n [see Eq. (3)]. Unfortunately, as we have indicated, the mass which enters μ_{In} may be a more complicated average.²⁶ However, following Blatt²¹ and Long and Myers²⁵ we use this as the mass in the ionized impurity scattering mobility. We thus obtain a correction term of the form

$$kT \left\{ \frac{d \ln A_n}{dP} + \frac{\mu_n}{\mu_{In}} \frac{d \ln \mu_{In}}{dP} \right\} \approx kT \left\{ \frac{3}{2} \frac{d \ln m_{\text{eff}}}{dP} - \frac{3}{8} \frac{d \ln m_{\text{eff}}}{dP} \right\} \\ = -0.8 \times 10^{-8} \text{ eV kg}^{-1} \text{ cm}^2.$$

In this way, we obtain

$$\frac{dE}{dP} = -5.4 \times 10^{-8} \text{ eV kg}^{-1} \text{ cm}^2, \\ \frac{d \ln m_{\text{eff}}}{dP} = -1.9 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2.$$

There is about 10% error in these values due to the measurements alone. The uncertainties due to the mobilities and assumptions regarding masses are difficult to estimate. Those due to the mobilities are at most 10%.

RESULTS AND INTERPRETATION: ACCEPTOR LEVELS

The study of aluminum and indium impurities in silicon by resistivity and Hall coefficient measurements as a function of temperature shows that the aluminum is de-ionizing below 70°K and the indium below 110°K. The activation energies are 0.057 and 0.16 eV, re-

spectively. Pressure measurements on samples containing these impurities were carried out at 49.5°K for aluminum-silicon and 90°K for indium-silicon so that both samples were in the range in which Eq. (4) is valid.

Figure 6 shows the normalized $\ln\rho$ vs pressure curve for an aluminum-doped silicon sample at 49.5°K and an indium-doped silicon sample at 90°K. For the aluminum-doped sample, the change in resistivity in 3000 kg cm⁻² corresponds to a temperature increment of $\sim 0.03^\circ\text{K}$; the error on each point is equivalent to a temperature fluctuation of $\pm 0.002^\circ\text{K}$. For the indium-doped sample, the change in resistivity in 5000 kg cm⁻² corresponds to a temperature of $\sim 0.05^\circ\text{K}$; the error on each point is equivalent to a temperature fluctuation of $\pm 0.003^\circ\text{K}$. From these data we obtain

$$\left. \frac{d \ln \rho}{dP} \right|_{\text{Al}} = 2.5 \times 10^{-6} \pm 10\% \text{ kg cm}^{-2} \text{ to } 5000 \text{ kg cm}^{-2},$$

$$\left. \frac{d \ln \rho}{dP} \right|_{\text{In}} = 6.7 \times 10^{-6} \pm 10\% \text{ kg cm}^{-2} \text{ to } 6000 \text{ kg cm}^{-2}.$$

If, as a first approximation, we neglect changes in A_p and μ_{pi} , then we obtain from Eq. (12),

$$dE(\text{Al})/dP = 1.0 \times 10^{-8} \pm 10\% \text{ eV kg}^{-1} \text{ cm}^2,$$

$$dE(\text{In})/dP = 5.2 \times 10^{-8} \pm 10\% \text{ eV kg}^{-1} \text{ cm}^2.$$

The information required to apply the exact corrections in Eq. (12) is not available, for the following reasons. The hole mobility is a complicated average that must take into account the complex nature of the warped valence band edge, and the presence of both lattice and ionized impurity scattering. Although the pressure coefficient of the lattice scattering mobility to 30 000 kg cm⁻² has been determined,³ it is not possible to analyze the data to separate the coefficients of the effective masses and the elastic constants. Thus, the coefficients of the parameters entering the ionized impurity and lattice mobility are unknown, and so also are the A_{pi} . Although these effects are all possibly small in absolute magnitude, they are also probably comparable to the effects actually measured in this experiment; this throws grave doubt on the interpretation of the change in ionization energy estimated without mobility and mass corrections. We can obtain some idea of the size of the corrections by making several assumptions about the changes in effective mass with pressure. Thus, if we first assume the ratio (m_1/m_2) pressure independent, the correction due to A_i and μ_i in Eq. (12) becomes

$$kT \left\{ \frac{d \ln m_1^{3/2}}{dP} + \frac{1}{(1+c)} \left[\frac{c\mu_1}{\mu_{I1}} + \frac{\mu_2}{\mu_{I2}} \right] \frac{d \ln (K^2/m_1^{1/2})}{dP} \right. \\ \left. + \frac{1}{(1+c)} \left[\frac{c\mu_2}{\mu_{I2}} + \frac{\mu_2}{\mu_{I2}} \frac{d \ln \mu_{2p}}{dP} \right] \right\}$$

TABLE II. Pressure coefficients of the ionization energies of various impurities in silicon.

Ionization energy (eV)	Type of level	Near band edge	Pressure coefficient (eV kg ⁻¹ cm ²)
1.16 ^a	gap		-1.5×10^{-6}
0.049	donor (As)	E_c	-5.4×10^{-8}
0.057	acceptor (Al)	E_v	$\sim +1 \times 10^{-8}$
0.16	acceptor (In)	E_v	$\sim +5 \times 10^{-8}$
0.35	donor (Au)	E_v	$< +5 \times 10^{-8}$
0.54	acceptor (Au)	E_c	-1.2×10^{-6}

^a G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. 111, 1245 (1958); and J. R. Haynes, M. Lax, and W. F. Flood, J. Phys. Chem. Solids 8, 392 (1959).

where $c = p_1\mu_1/p_2\mu_2$. If now, in addition, we apply the coefficient found for μ_{2p} at room temperature by Smith,³ and also assume the changes in the m_i are the same as for the electron effective masses ($\sim -2 \times 10^{-6}$ kg⁻¹ cm²), we obtain

$$dE(\text{Al})/dP = 1.3 \times 10^{-9} \text{ eV kg}^{-1} \text{ cm}^2,$$

$$dE(\text{In})/dP = 3.8 \times 10^{-8} \text{ eV kg}^{-1} \text{ cm}^2.$$

If, on the other hand, we were to assume

$$d \ln m_i/dP = +2 \times 10^{-6} \text{ kg}^{-1} \text{ cm}^2,$$

we should obtain

$$dE(\text{Al})/dP = 1.8 \times 10^{-8} \text{ eV kg}^{-1} \text{ cm}^2,$$

$$dE(\text{In})/dP = 5.8 \times 10^{-8} \text{ eV kg}^{-1} \text{ cm}^2.$$

Thus, we conclude that the exact numerical coefficients we obtain do not have very much significance. The fact that they are small and remain small for physically plausible mobility and mass corrections is significant. The slightly larger coefficient for indium is also established beyond experimental error.

CONCLUSIONS

The changes with pressure of the ionization energies of the group V and group III impurities in silicon are of the order of 10^{-8} eV kg⁻¹ cm². This is to be compared with the pressure coefficient of the intrinsic energy gap for this material of -1.5×10^{-6} eV kg⁻¹ cm².⁵ The donor energy level measured moves towards the conduction band edge while both acceptor levels measured appear, with less certainty, to move away from the valence band edge. For comparison, the "deep" lying gold impurity level near the center of the silicon energy gap moves toward the conduction band edge at a rate of 1.2×10^{-6} eV kg⁻¹ cm² (see paper II of this series). Also, the energy levels caused by gold in germanium similarly have pressure coefficients of the order of 10^{-6} eV kg⁻¹ cm² (see paper III of this series). The pressure coefficients of the levels in silicon are summarized in Table II.

The pressure coefficient of the ionization energy of the arsenic donor impurity can be explained in terms of the changes in effective mass and dielectric constant

with pressure. In principle, the change in effective mass of the electrons may be calculated from the changes in the electron energy eigenvalues at the momentum corresponding to the band edge; unfortunately, these are not yet all known.

As the theory of impurity levels near the degenerate, warped valence-band edge does not give an analytical expression for the ionization energy, we cannot readily interpret the results in terms of the change in dielectric constant and effective mass with pressure. If this ionization energy were described by a hydrogenic picture, they would indicate a small decrease (less than 0.5% in $10\,000\text{ kg cm}^{-2}$) in effective mass with pressure.

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Effect of Pressure on the Energy Levels of Impurities in Semiconductors. II. Gold in Silicon*†

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The changes in resistivity of silicon samples containing gold impurity, which are appropriately counter-doped with hydrogenic impurities, have been measured at hydrostatic pressures up to $30\,000\text{ kg cm}^{-2}$ near room temperature. The changes are explained by a dependence on pressure of the ionization energy of the gold impurity.

The pressure coefficient of the energy of a gold acceptor level near the center of the forbidden gap has been determined, relative to both band edges; the coefficient of the separation from the conduction band edge is twice that of the separation from the valence band. The sum of the two coefficients gives a pressure coefficient for the total energy gap of $-1.5 \times 10^{-6}\text{ eV kg}^{-1}\text{ cm}^2$ between 0 and 4000 kg cm^{-2} or $-2.4 \times 10^{-6}\text{ eV kg}^{-1}\text{ cm}^2$ near $20\,000\text{ kg cm}^{-2}$. The low-pressure value is in agreement with previous, more direct, determinations. A donor level due to the gold, roughly 0.35 eV above the valence band edge, has a very low pressure coefficient relative to that edge.

INTRODUCTION

IN the first paper of this series, we considered the effect of hydrostatic pressure on the energy levels of the so-called hydrogenic impurities in silicon. These energy levels are well understood at atmospheric pressure, and the small pressure effects found are easily explained. Most other impurities give rise to energy levels distributed throughout the forbidden energy gap and are poorly understood. It is possible that measurement of the ionization energy of an impurity level, as a function of the lattice constant of the host crystal, will yield additional useful information about the properties of the impurity and of the host crystal. Gold alloyed with silicon would appear to be suitable for such an investigation since it yields deep-lying levels,

and can be introduced into the host lattice in relatively large concentrations.

Some of the physical properties of gold-doped silicon have been extensively investigated.¹⁻⁶ The measurements of electrical resistivity and Hall effect as a function of temperature established that gold produces at least two energy levels in the forbidden energy gap, one an acceptor level 0.54 eV below the conduction band edge, and the other a donor 0.35 eV above the valence band edge, at the absolute zero of temperature.⁶ The energy level diagram as determined by Collins, Carlson, and Gallagher⁶ is shown in Fig. 1. E_a is the gold acceptor level energy, E_d the donor level energy, E_c the

¹ E. A. Taft, and F. H. Horn, *Phys. Rev.* **93**, 64 (1954).

² F. J. Morin, J. P. Maita, R. Shulman, and N. B. Hannay, *Phys. Rev.* **96**, 833 (1954).

³ J. A. Burton, *Physica* **20**, 845 (1954).

⁴ C. B. Collins, and R. O. Carlson, *Bull. Am. Phys. Soc.* **1**, 127 (1956).

⁵ R. O. Carlson, C. B. Collins, and C. J. Gallagher, *Bull. Am. Phys. Soc.* **1**, 128 (1956).

⁶ C. B. Collins, R. O. Carlson, and C. J. Gallagher, *Phys. Rev.* **105**, 1168 (1957).

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† A preliminary account of this work has been given in *Bull. Am. Phys. Soc.* **2**, 134 (1957).

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