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 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 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 -1.5×10^{-6} eV kg^{-1} cm^2 between 0 and 4000 kg cm^{-2} or -2.4×10^{-6} eV kg^{-1} cm^2 near 20 000 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 Gallagher[6] is shown in Fig. 1. E_a is the gold acceptor level energy, E_d the donor level energy, E_c the

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

TABLE I. Atmospheric pressure data on samples measured.

Crystal	Concentration of gold (cm^{-3})	Major compensating impurity	Major compensating impurity concentration $\lvert N_d-N_a\rvert$ (cm^{-3})	Ionization energy (eV)	Crystal type	De-ionizing level	Temperature of measurement (°K)
C-D-2	8×10^{16}	Group V	10^{14}	$E_a-E_v=0.62$	p	Acceptor	297
C-Si-309	1.6×10^{15}	Group V	4×10^{14}	$E_c-E_a=0.54$	n	Acceptor	297
C-Si-308	4×10^{14}	Group III	2×10^{14}	$E_d-E_v=0.35$	p	Donor	195

conduction band edge energy, and E_v the valence band edge energy.

Collins, Carlson, and Gallagher also noted that appropriate counter-doping of a silicon crystal with group V impurities allowed observation of the 0.54-eV acceptor level either as a source of electrons in an n-type crystal or as a sink for electrons in a p-type crystal. Resistivity and Hall effect measurements were made as a function of temperature on the n- and p-type crystals; these gave ionization energies that were, respectively, the distances of the level from the conduction and valence band edges at absolute zero. The sum of the ionization energies gives a value for the forbidden energy gap at absolute zero in satisfactory agreement with the previously determined value of 1.21 eV.[7] Pressure measurements of the resistivity of n- and p-type samples, at the appropriate temperature, can be interpreted to give the pressure coefficients of the acceptor level relative to either band edge, and the pressure coefficient of the total forbidden gap. The pressure coefficient of the donor level relative to the valence band edge can be found from a separate measurement on a suitable p-type sample.

EXPERIMENTAL RESULTS

The experimental techniques and procedures have been described in detail elsewhere.[8] The manganin gauge used for pressure measurement was calibrated by assuming that the freezing pressure of mercury at 0°C was 7640 kg cm^{-2}.

The doping of the three silicon samples used is given in Table I. The concentrations of gold impurity and group III or group V compensating impurity were determined from measured additions to the silicon melt and from solubility data.[6] The ionization energies are those determined by Collins, Carlson, and Gallagher[6] (from resistivity and Hall effect measurements) on samples cut from the same crystals as ours; resistivity vs $1/T$ plots in this laboratory are consistent with these ionization energies.

Since crystals C-D-2 and C-Si-309 were still in the de-ionizing range at room temperature, it was possible to perform pressure measurements on them in the 30 000 kg cm^{-2} apparatus; the results are shown in Figs. 2 and 3. Sample C-Si-308 was, however, completely ionized above 0°C; measurements on it were restricted to 7000 kg cm^{-2} at 0°C and at −78°C in the gas apparatus. The results at −78°C are shown in Fig. 4.

The ordinate for the curves of experimental results is $\ln(\sigma/\sigma_0)$, where σ_0 is the conductivity at atmospheric pressure and σ that at high pressure. No correction has been made for dimensional changes, which introduce only a 1% difference in the conductivity by 30 000 kg cm^{-2}

The conductivity of sample C-D-2 increases by nearly a factor of 2 in 24 000 kg cm^{-2} with an increasing slope at the high pressure limit. At a fixed pressure, and after the temperature has settled to a constant value, there is a slow but small change of the conductivity with time. This is indicated by the direction of the arrows in Figs. 2 and 3.

The conductivity of sample C-Si-309 increases by 4 to 5 times in 27 000 kg cm^{-2}, with only little evidence of curvature. Again slow time effects were observed. A second experiment on this sample was carried out in the gas apparatus, at room temperature, and 7000 kg cm^{-2}. The results agreed with those in the other apparatus. However, temperature fluctuation made the observation of time-dependent effects impossible.

The results for sample C-Si-308 show that the conductivity change is less than 2% to 7000 kg cm^{-2} at −78°C. Measurements at 0°C tend to agree with this; however, inferior temperature regulation prevented exact confirmation. Time-dependent effects were not observable because of temperature fluctuations.

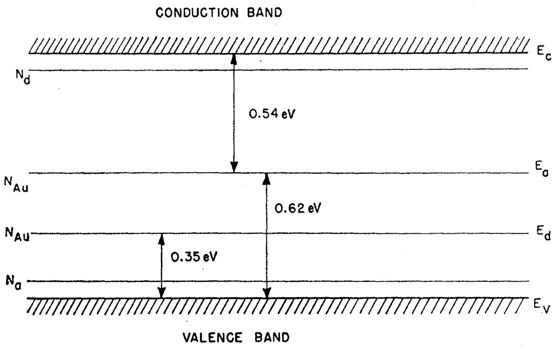

FIG. 1. Energy-level diagram for gold-doped silicon.

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[7] See, for example, F. J. Morin, and P. J. Maita, Phys. Rev. **96**, 28 (1954).

[8] W. Paul, and H. Brooks, Phys. Rev. **94**, 1128 (1954).

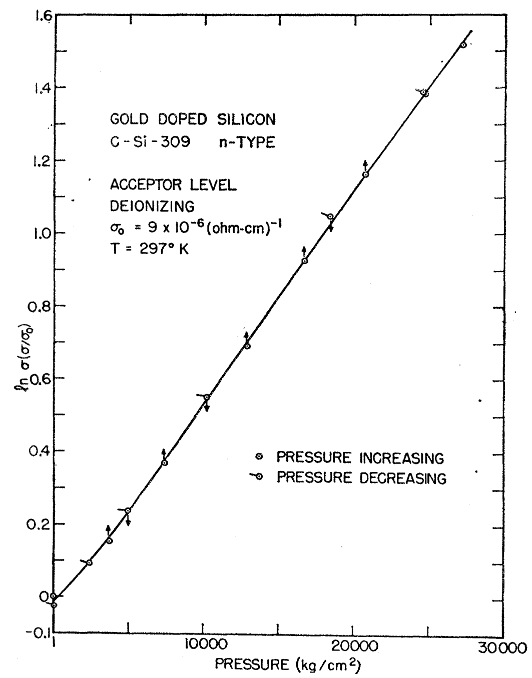

FIG. 2. Pressure dependence of the conductivity of a gold-doped silicon sample with the acceptor level de-ionizing into the conduction band.

DISCUSSION

In interpreting our results we shall assume that the electron and hole mobilities are independent of pressure. This assumption is based on conductivity measurements made in this laboratory[9] on silicon doped with group III and group V impurities at a temperature such that the number of carriers is independent of pressure. These measurements show that the carrier mobilities in the presence of lattice scattering increase only about 3% in 10 000 kg cm^{-2}. Moreover, measurements by Cardona, Paul, and Brooks[10] show that the dielectric constant of silicon changes approximately 1% in 10 000 kg cm^{-2}. Therefore, it is most likely that the ionized impurity scattering mobility does not change much with pressure. These two scattering mechanisms are probably the dominant ones in our crystals. However, unless there is a high degree of compensation in our samples, other scattering mechanisms are important, since the Hall mobilities measured by Collins, Carlson, and Gallagher[6] in these crystals appear to be somewhat lower than those found by other workers[7] in silicon crystals with comparable densities of ionized impurities. Nevertheless, we ignore any dependence of the mobility on pressure.

At the temperatures at which the pressure measurements were carried out the conductivity of the samples is given by

$$\sigma = \mu e A \exp(-E_i/kT), \tag{1}$$

where μ is the majority carrier mobility, e is the electronic charge, A is a function of the effective mass and the impurity densities, k is Boltzmann's constant, T is the absolute temperature, and E_i is the ionization energy given in Table I.

Using the data of Figs. 2, 3, and 4, we can determine from Eq. (1) the pressure dependences of the ionization energies given in Table I provided that the effective masses and mobilities do not change. We find

$$\begin{aligned} d(E_c-E_a)/dP &= (-1.2\pm0.1)\times10^{-6}\ \text{eV kg}^{-1}\text{cm}^2, \\ &\qquad 0\text{–}4000\ \text{kg cm}^{-2} \\ &= (-1.5\pm0.1)\times10^{-6}\ \text{eV kg}^{-1}\text{cm}^2, \\ &\qquad \text{near } 20\,000\ \text{kg cm}^{-2}, \end{aligned} \tag{2}$$

$$\begin{aligned} d(E_c-E_v)/dP &= (-0.3\pm0.25)\times10^{-6}\ \text{eV kg}^{-1}\text{cm}^2, \\ &\qquad 0\text{–}4000\ \text{kg cm}^{-2} \\ &= (-0.9\pm0.1)\times10^{-6}\ \text{eV kg}^{-1}\text{cm}^2, \\ &\qquad \text{near } 20\,000\ \text{kg cm}^{-2}, \end{aligned} \tag{3}$$

$$|d(E_d-E_v)/dP| < 0.05\times10^{-6}\ \text{eV kg}^{-1}\text{cm}^2, \quad 0\text{–}7000\ \text{kg cm}^{-2}. \tag{4}$$

The errors give an estimate of the deviations of the experimental points from the curves. Combining Eqs. (2) and (3) we find for the total forbidden gap $E_g = E_c - E_v$:

$$\begin{aligned} dE_g/dP &= -1.5\times10^{-6}\ \text{eV kg}^{-1}\text{cm}^2, \\ &\qquad 0\text{–}4000\ \text{kg cm}^{-2} \\ &= -2.4\times10^{-6}\ \text{eV kg}^{-1}\text{cm}^2, \\ &\qquad \text{near } 20\,000\ \text{kg cm}^{-2}. \end{aligned} \tag{5}$$

In both samples, C-D-2 and C-Si-309, slow drift of the conductivity with time was observed under conditions of constant temperature and pressure. The constancy of the pressure was judged by the readings of the manganin wire gauge. The constancy of the temperatures was inferred from our previous experience with this apparatus and, particularly, from the fact that in one of the experiments a germanium sample was included right next to the silicon sample as a very sensitive thermometer. The drifts are indicated by directions noted in Figs. 2 and 3. The conductivity tended to increase after an increase in pressure and to decrease after a decrease in pressure. The time constants involved were of the order of hours. In sample C-D-2 the amount of the drift during a normal observation interval was of the order of 2% of the conductivity, and in sample C-Si-309 of the order of 0.5%. The conductivity of any sample is almost the same when measured on increasing or decreasing the pressure. We feel that the slight hysteresis loop displayed by sample C-D-2 would have closed if the conductivity had been followed to its terminal value at each pressure. This was not practicable because of the long times involved. The crossing of the increasing and decreasing pressure curves is

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[9] A. C. Smith, Technical Report H.P.2, Gordon McKay Laboratory, Harvard University, 1958 (unpublished).

[10] M. Cardona, W. Paul, and H. J. Brooks, J. Phys. Chem. Solids, 8, 204 (1959).

probably due to an over-all temperature change of 1°C between the start and finish of the experiment.

When the pressure is increased or decreased, there is introduced a positive or negative temperature pulse which dies away in a time of the order of 10 min. We decided to try to separate the effects of the pressure and temperature changes by immersing the sample in isopentane (the pressure transmitting fluid used in the pressure experiment), applying to it a positive or negative temperature pulse, and subsequently observing any change in the conductivity with time.

For this experiment the silicon sample C-D-2, which showed the largest time-dependent effects, was mounted on a copper holder along with an intrinsic sample of germanium. Samples and holder were inserted in a test tube. The test tube was placed temporarily in a bath of hot or cold water, transferred to another bath and then held at a constant intermediate temperature of 23.8°C. The temperature control was better than ±0.03°C for short periods of time as indicated by our previous experiments with an intrinsic germanium sample. The conductivity of the germanium sample in this experiment indicated that the samples and copper block came to equilibrium in the bath in 10 min or so. No drifts of the silicon conductivity were observed after this time. We conclude that the drifts are probably caused by the pressure effect alone, and that the temperature pulse in the pressure apparatus is not a vital factor.

Although our results are far from conclusive on any mechanism for the long-time trapping, we shall discuss briefly several possible phenomena we have considered. The absence of long-time effects after the positive and negative temperature pulses is evidence against explaining the effects on the basis of filling and emptying bulk traps of constant density in the crystals. Moreover, it also seems likely that if the pressure experiment time effects are allied with surface conductivity phenomena, positive and negative temperature pulses ought to cause some observable effect. However, we do not feel that these experiments alone exclude surface effects.

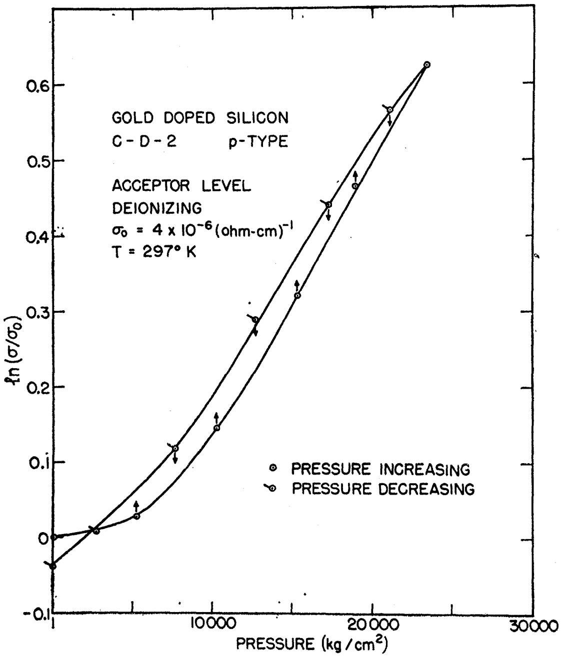

Fig. 3. Pressure dependence of the conductivity of a gold-doped silicon sample with the acceptor level de-ionizing into the valence band.

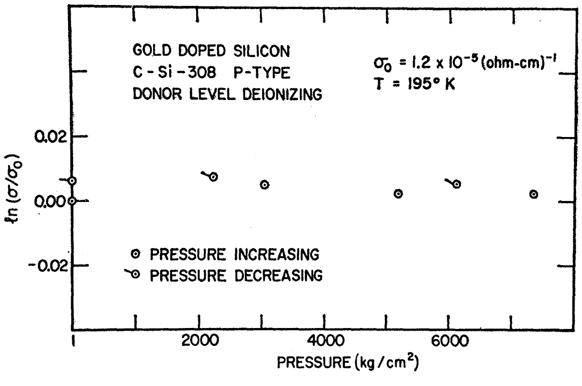

Fig. 4. Pressure dependence of the conductivity of a gold-doped silicon sample with the donor level de-ionizing into the valence band.

We might speculate that the time-dependent effects may be due to a change with pressure of the density of a level in the forbidden gap (whether caused by dislocation movement, impurity diffusion, vacancy creation or other mechanism, we cannot say), and that these changes occur slowly. If the effect is mechanical in nature, i.e., due to dislocations or similar defects, crystals grown in the same laboratory at about the same time might be expected to exhibit similar behavior. However, if the cause is tied to impurity diffusion from one type of site to another, the time-dependent effect may be different in differently doped but similarly grown samples. There is some additional experimental evidence on this point. Paul and Pearson[11] reported similar time effects in early samples of silicon from Bell Laboratories. The present experiments were carried out on samples from the General Electric Research Laboratory. Holland[12] has observed very large (of the order of 50% of the conductivity) similar effects in a silicon sample from General Electric but doped with manganese. The very much larger effect in the manganese-doped sample might seem to indicate a dependence of the time effect on the impurity doping.

SUMMARY

We have deduced from resistivity measurements at room temperature a value for the total energy gap

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[11] W. Paul and G. L. Pearson, Phys. Rev. **98**, 1755 (1955).

[12] M. G. Holland, Technical Report H.P.4, Gordon McKay Laboratory, Harvard University, 1958 (unpublished).

change with pressure of -1.5×10^{-6} eV kg^{-1} cm^2 in a low-pressure region. This is in satisfactory agreement with the determination of Paul and Pearson[11] of -1.5×10^{-6} eV kg^{-1} cm^2 and of Warschauer and Paul[13] of approximately -1.3×10^{-6} eV kg^{-1} cm^2. Above 10 000 kg cm^{-2} we find that the total energy gap is decreasing rather more rapidly with pressure; an approximate value for this change at 20 000 kg cm^{-2} is -2.4×10^{-6} eV kg^{-1} cm^2. The error on both the 1.5 and 2.4 figure for the gap change is $\pm0.3\times10^{-6}$ eV kg^{-1} cm^2. We find that the change with pressure of $E_c-\mathrm{E}_a$ is -1.2×10^{-6} eV kg^{-1} cm^2 with a slight tendency to curvature which brings the value up to -1.5 at the highest pressure. The change of $|E_v-E_a|$ is at the rate of -0.3×10^{-6} eV kg^{-1} cm^2 with more definite positive curvature increasing the value to around -0.9×10^{-6} eV kg^{-1} cm^2 at the higher pressures. The change of $|E_v-E_d|$ is less than 5×10^{-8} eV kg^{-1} cm^2, the measurement being done only to 7000 kg cm^{-2}. From these results we infer that the donor gold level remains essentially fixed with respect to the valence band edge. The acceptor level almost in the center of the forbidden energy gap moves with respect to both valence and conduction band edges, but considerably more with respect to the conduction band edge. This "tying" of the gold impurity levels to the valence band edge is similar to what is found in germanium doped with gold.[14]

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[13] D. M. Warschauer and W. Paul, J. Phys. Chem. Solids, **5**, 102 (1958).

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