Pressure Dependence of the Resistivity of Silicon

WILLIAM PAUL, *Division of Applied Science, Harvard University, Cambridge, Massachusetts*

AND

G. L. PEARSON, *Bell Telephone Laboratories, Murray Hill, New Jersey*

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The variation of resistivity of high-purity single crystals of silicon has been measured as a function of hydrostatic pressure in the intrinsic range. The results are interpreted to give a decrease in energy gap between conduction and valence bands with applied pressure.

THE variation of resistivity of silicon crystals with hydrostatic pressure has been previously reported by Bridgman.[1] His measurements were made on relatively impure n- and p-type crystals up to 30 000 kg/cm^2 at room temperature. The resistivity showed marked hysteresis in a pressure cycle, which made it difficult to deduce the intrinsic behavior of the silicon. It was clearly necessary to measure the resistivity as a function of pressure in the intrinsic range of conductivity of purer samples, as they became available. The purpose of this note is to describe such experiments at pressures up to 7000 kg/cm^2.

APPARATUS

The pressure apparatus used is that developed by Bridgman[2] and yields pressures up to 7000 kg/cm^2 at temperatures up to 350°C, if one uses nitrogen, argon, or helium as transmitting gas. The pressure is measured with a manganin gauge. The pressure bomb was immersed in a bath of silicone oil whose temperature could be controlled to 0.03°C by a thyratron controller. The resistance variation due to temperature fluctuation was small compared to the effect of the pressure application. There is, however, a temporary change in temperature when the pressure is altered, and this change will be important if long time-constant trapping can take place in the sample (see Paul and Brooks[3] for this and further experimental details). No pressure run was started until the controller had been at its regulating temperature, and the resistance of the sample had remained constant, for an hour or more.

The n-type single crystals used had room temperature resistivity of 400 ohm-cm and became intrinsic around 130°C. The contacts to the silicon were of 0.25-mm gold wire bonded to the silicon in a 0.5-mm diameter bond. The crystals were some 2 cm long by 0.1 cm square. The current through the samples was between 5 and 20 microamperes. Readings of the resistivity, by a potentiometric method, were taken for both increasing and decreasing pressure, care being taken that temperature equilibrium had been re-established after each alteration of pressure.

[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **79**, 142 (1951).
[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, 157 (1932), and Proc. Am. Acad. Arts Sci. **82**, 71 (1953).
[3] W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).

RESULTS

The resistivity ρ of an intrinsic semiconductor is given by

$$\rho = (1/e)[1/(\mu_e+\mu_p)](1/2A)\exp(E_g/2kT),$$

where μ_e and μ_p are the electron and hole mobilities, E_g the energy gap, and A is given by $A=(2\pi kT/h^2)^{\frac{3}{2}}\times(m_em_p)^{\frac{3}{4}}$, where m_e and m_p are the effective masses for electrons and holes respectively. If we assume that the effective masses are independent of pressure (which is not necessarily accurate), then any change in intrinsic resistivity at fixed temperature is probably the net effect of a change in the energy gap E_g and the carrier mobilities μ_e and μ_p. The latter are usually determined from the resistivity *vs* pressure curves at low temperatures on fairly impure n- and p-type samples, where the (single-type) carrier density remains constant with pressure if the carriers are derived from shallow impurity levels.[4]

The experimental results for sample Si VI-270 are summarized in Fig. 1. The quoted resistivities were derived from the measured resistances at high pressure and high temperature and the dimensions at atmospheric pressure and room temperature. The error involved in disregarding any changes in dimensions of the crystals with pressure and temperature is small. The circles denote the zero-pressure resistivities, the crosses the resistivities at 6000 kg/cm^2. In the intrinsic range of conduction the resistivity has decreased with the increase in pressure, in the opposite direction to the behavior in germanium.[3]

The detailed pressure variation of resistivity for Si VI-270 at various temperatures is shown in Fig. 2; similar behavior is found for other n-type samples of the same resistivity. At the highest temperatures, in the intrinsic range, the resistivity variation is essentially linear and reversible. The slope of the resistivity *vs* pressure curve at the high-pressure end decreases slightly as the temperature is lowered and the onset of the "intrinsic" slope moves to higher pressures. At still lower temperatures, there is little over-all change of resistivity with pressure. We consider that the high-

[4] An argument for the germanium case, showing that the ionization of shallow levels is unlikely to be affected by pressure, is given by W. Paul and H. Brooks, reference 3.

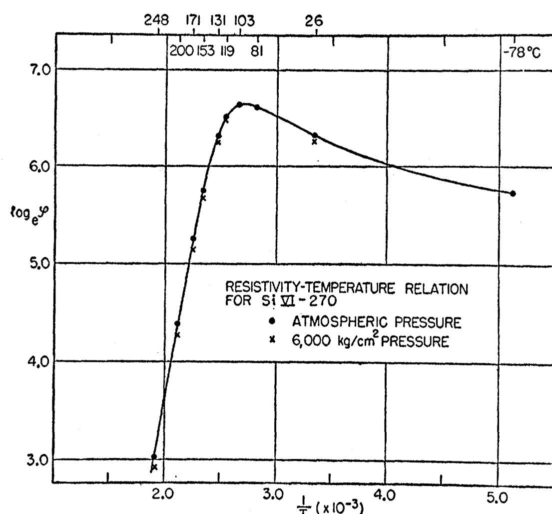

FIG. 1. Resistivity in ohm-cm *versus* reciprocal of temperature curve for Si sample VI-270 at two pressures.

temperature resistivity decrease with the pressure is an intrinsic property of the silicon, corresponding to decrease in the energy gap between conduction and valence bands. The existence of a break—although not sharp—in the resistivity *vs* pressure curves at intermediate temperatures and the shift in its position with temperature agrees with this supposition. The smaller rate of resistivity decrease at lower temperatures is consistent with the view that there is a higher proportion of impurity-derived electrons and that the concentration of these is less affected by the applied pressure. The uniform decrease of resistivity with pressure in the intrinsic range would give $(\partial E_g/\partial p)_T = -1.5\times10^{-12}$ ev per dyne/cm² at 250°C, *in the absence of any mobility changes.*

DISCUSSION

There are, however, some anomalous effects at the lower temperatures, and especially at low pressures. The points plotted in Fig. 2 represent the value of the resistance when it is estimated that the temperature has re-settled to its equilibrium value after a change in pressure. The change in the manganin gauge reading with time is one criterion for this re-establishment of temperature equilibrium, and past experience with the identical apparatus and trap-free germanium crystals provides additional good evidence for the equilibrating time. The resistivity determined in this way drops sharply on the initial application of pressure then flattens before finally going over into the intrinsic decrease. There is, also, hysteresis in this low-pressure region on relieving the pressure. Further, at fixed temperature and pressure there can occur slow changes of resistance with time, both on the outgoing and incoming pressure curves. The trend of the resistance away from the "initial" value is indicated by an arrow for some of the graph points. When the pressure is

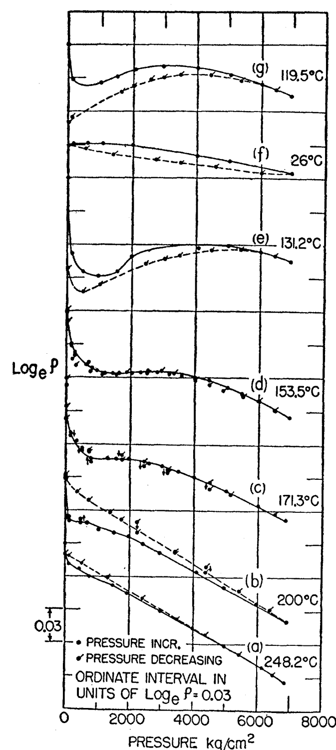

FIG. 2. Resistivity in ohm-cm *versus* pressure curve for Si sample VI-270 at various temperatures. The zero-pressure points (•) on the curves have the following values of $\log_e\rho$: (a) 3.03, (b) 4.39, (c) 5.27, (d) 5.75, (e) 6.29, (f) 6.325, (g) 6.51.

finally reduced to zero the resistivity is normally lower than it was before the run. If the temperature be maintained over an hour or two, the resistivity steadily increases to a value near its pre-run value.

It is likely that these hysteresis and time dependent effects are caused by an alteration with pressure of the density, or the electron occupation density, of deep lying traps[5] in the crystal, and with the temporary temperature change accompanying a change in pressure. The resistivity *vs* pressure curve obtained at low temperature, if one waited for trap equilibrium to be re-established after each temperature-pressure change, would probably be reversible but would not give the variation in electron mobility which is what is wanted from low-temperature experiments. *P*-type crystals that have been examined[6] thus far also show trapping effects which prevent the determination of the change in hole mobility with pressure. The mobility changes, and the correction to $(\partial E_g/\partial p)_T$ resulting, really require trap-free crystals although it might be possible to keep the traps filled at all pressures by suitable infrared irradiation. It is probable that the crystals examined by Bridgman, which gave wide resistance-pressure loops, contained traps, and perhaps even pressure-created traps.

[5] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).
[6] In conjunction with G. B. Benedek.

The experiments described have been carried out in argon, nitrogen, and helium gases, with no significant difference in the results obtained. Additional work in isopentane to 30 000 kg per cm^2 at room temperature seems to suggest a small increase in the electron mobility with pressure, but the trapping effects make this less certain. However, no violent change in the electron mobility such as has been found for germanium[3] was observed. It must be emphasized that the trap effects which mask the mobility changes are not important at the highest temperatures, so that the decrease in resistivity with pressure there is genuine, and the deduction of an energy gap decrease with pressure could be invalidated only by improbably large increases in one or both of the carrier mobilities. The results reported here have been checked by examining the change in the optical absorption edge with pressure, up to 8000 kg/cm^2. The shift in the edge is towards longer wavelengths, or smaller energies, and is of about the same magnitude as in the above experiments.[7] It is intended to further check the results by examining the change in Hall mobility of electrons and holes with pressure.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the helpful advice given by Professor H. Brooks on all aspects of this investigation, and the assistance of Professor P. W. Bridgman in making available his apparatus and experience in high-pressure measurements.

[7] Warschauer, Paul, and Brooks, Bull. Am. Phys. Soc. **30**, No. 1, 54 (1955).

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Optical and Impact Recombination in Impurity Photoconductivity in Germanium and Silicon

N. SCLAR AND E. BURSTEIN
United States Naval Research Laboratory, Washington, D. C.
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The impact (three-body) recombination and optical recombination coefficients are calculated for hydrogen-like impurity centers in extrinsic germanium and silicon in thermal equilibrium. These have been compared with the phonon recombination coefficient calculated by Gummel and Lax for a similar model. It is found that the optical coefficient is always less than the phonon coefficient in the temperature range of interest. The impact ionization coefficient which is proportional to the free carrier concentration may be comparable with or greater than the phonon recombination coefficient at 4.2°K in the presence of background radiation and definitely exceeds it at higher temperatures. Comparison with experimental data indicates that none of the mechanisms considered can yet explain the observed time constants.

IN phenomena involving deviations from the free charge carrier equilibrium concentration in semiconductors, there are generally several different mechanisms that tend to bring the system back to equilibrium. The time constant for the phenomenon will depend on which mechanism is dominant in effecting the return to equilibrium. The purpose of this note is to analyze the mechanisms contributing to the time constant for impurity photoconductivity in extrinsic semiconductors. This is accomplished by comparing the various recombination coefficients calculated on the basis of a simplified model. The recombination coefficients considered to be of importance are B_p, B_0 and B_In. B_p is the phonon (nonradiative) recombination coefficient which consists of recombination with the emission of phonons; B_0 is the optical (radiative) recombination coefficient which consists of recombination with the emission of photons, and B_In is the impact (three-body) recombination coefficient which consists of recombination with the excitation of a second free carrier, i.e., the inverse of impact ionization. The simplified model used consists in representing the impurity centers as hydrogen-like. The bound charge carrier of effective mass m^* is considered to exist in a stationary state about the impurity ion under the influence of a net unit charge reduced by the dielectric constant of the medium. By using this model, the optical (radiative) and impact (three-body) recombination coefficients are calculated and compared with the phonon (nonradiative) coefficient calculated by Gummel and Lax for a similar model. Unfortunately, none of the mechanisms considered can yet explain the short time constants found experimentally.

Impurity photoconductivity due to the photoionization of bound charge carriers at neutral impurity centers is observed at low temperatures in germanium and silicon doped with elements from the III and V columns of the periodic table.[1,2] Under conditions of small signals, where deviations from the equilibrium concentration of charge carriers are small and where thermal equilibrium between the charge carriers and the lattice

[1] Burstein, Oberly, and Davisson, Phys. Rev. **89**, 331 (1953).
[2] V. B. Rollin and E. L. Simmons, Proc. Phys. Soc. (London) **B65**, 995 (1952); Burstein, Davisson, Bell, Turner, and Lipson, Phys. Rev. **93**, 65 (1954).