

Absorption of Light in Alpha SiC near the Band Edge

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The absorption in alpha SiC of photons of energy 2.6 ev to 3.3 ev has been measured at temperatures from 77°K to 717°K. The measurements show that the interband transitions are indirect, requiring the absorption or emission of a phonon of energy 0.09 ev. The minimum energy gap is found to be 2.86 ev at 300°K, and above this temperature $dE_G/dT = -3.3 \times 10^{-4}$ ev/degree.

INTRODUCTION

IN cubic (beta) SiC the conduction band minima are expected to be along [100] axes as in Si and diamond, with valence band maximum at $k=0$. Hence indirect interband transitions should be expected near the band edge,¹ with simultaneous absorption or emission of a phonon. The hexagonal (alpha) SiC lattices have interatomic distances very nearly the same as the cubic, but differ in the ordering of the close-packed planes. We do not know how this affects the energy band structure, but the fact that the absorption can be interpreted according to the scheme of Macfarlane and Roberts² shows that indirect transitions are being observed.

Macfarlane and Roberts use the formula

$$\alpha = A \left[\frac{(h\nu - E_G + k\theta)^2}{e^{\theta/T} - 1} + \frac{(h\nu - E_G - k\theta)^2}{1 - e^{-\theta/T}} \right], \quad (1)$$

where α is the absorption constant in cm^{-1} , $h\nu$ is the photon energy, E_G is the minimum energy gap, $k\theta$ is the energy of the phonon absorbed or emitted, and A is a constant depending on properties of the material and the electron-phonon interaction. The two terms give the contributions due to phonon absorption and emission, respectively. These terms give separate linear contributions in a plot of $\alpha^{1/2}$ vs photon energy, with an energy difference $2k\theta$ between intercepts on the energy axis (see Fig. 1). In addition θ determines the relative slopes of the two lines. The fact that these two relations must be satisfied simultaneously by a choice of θ clearly shows whether or not the theory of indirect transitions is applicable to the experimental data.

EXPERIMENTAL PROCEDURES

Two methods of measuring the absorption were employed. One was the conventional in-out transmission method, using a thin (95μ) clear plate of SiC. Chopped monochromatic radiation was used, with a 1P28 photomultiplier as detector. The reflectivity was computed from the values of the index of refraction given by Weigel.³ By comparison with the other method to be

described it was felt that the values of α obtained this way were reliable in the range from 70 cm^{-1} to 500 cm^{-1} . Although we tried many samples, the impurity absorption always prevented us from obtaining reliable data in the region of small α .

In order to make an adequate interpretation using the Macfarlane and Roberts scheme, it was essential to measure absorption constants down to $\alpha \sim 10 \text{ cm}^{-1}$. We therefore used a second method in which our samples were SiC crystals of the light-emitting variety. They have p - n junctions a few microns below the surface⁴ and can therefore be used as both absorber and detector. We measured the photovoltage developed when a known amount of chopped light from the monochromator fell on the surface. This voltage should be proportional to the absorption constant for small photovoltages and

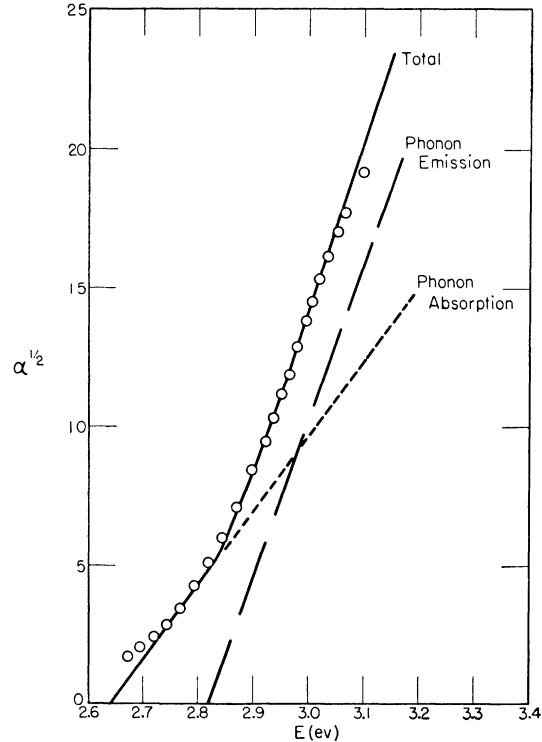


FIG. 1. Comparison of observed and calculated absorption at 700°K.

¹ Bardeen, Blatt, and Hall, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954* (John Wiley and Sons, Inc., New York, 1956), p. 146.

² G. G. Macfarlane and V. Roberts, *Phys. Rev.* **97**, 1714 (1955); **98**, 1865 (1955).

³ O. Weigel, *Nachr. Ges. Wiss. Göttingen*, 264 (1915).

⁴ Lyle Patrick (to be published).

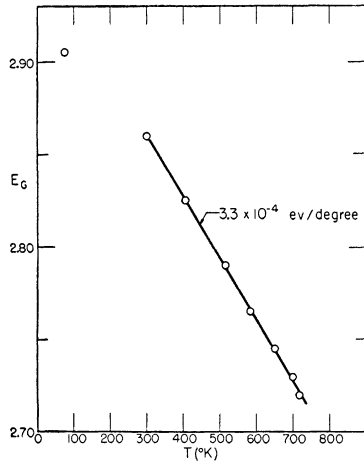


FIG. 2. E_G vs T for α SiC.

small absorption constants. The advantage in using junctions is that no signal is observed unless electron-hole pairs are created near the junction, hence we were able to avoid the impurity absorption which hid the lower part of the curve in the transmission data.

The limitation on photovoltage is that it should be in the region in which the forward characteristic of the p - n junction is linear. In practice some nonlinearity was introduced by the sample contacts, but curves of signal vs light intensity for a given wavelength enabled us to make the necessary corrections. The limitation to small absorption constants may be seen from the formula for "quantum efficiency" developed by Pfann and van Roosbroeck⁵ for p - n junction power sources. Their formula shows that for the purposes of these measurements a small diffusion length, L , is advantageous because it extends the linear region to larger α . In SiC, L is a few microns and we were able to measure up to $\alpha \sim 300$ before the nonlinearity became appreciable; this value is roughly that expected from the formula when our best estimates of the parameters are used.

By this method the relative signal as a function of wavelength for a given number of photons can be accurately measured, but there are too many unknowns to express the result in terms of the absorption constant α . Hence the transmission measurements in the range in which they were dependable were used to adjust the junction measurements to an absolute scale. After this adjustment the two sets of measurements very nearly coincided over a considerable range of α (from about 70 cm^{-1} to 350 cm^{-1}). At higher values of α , both methods become less accurate.

The experiments were repeated with several other p - n junctions at several temperatures but no differences in results were observed.

For measurements at and above room temperature the junctions were mounted in a Lavite block which had imbedded in it a calibrated chromel-alumel thermo-

couple. At liquid nitrogen temperature the junctions were placed in a brass block which was totally immersed in the coolant. The radiation was chopped at 33 cycles and supplied by a 300-watt zirconium source, 100-watt tungsten ribbon, or a 1000-watt mercury arc, all in conjunction with a grating monochromator. The beam was monitored at all times by a calibrated photocell.

RESULTS

In Fig. 1 we show two lines representing phonon absorption and phonon emission at 700°K as calculated from formula (1) with $\theta = 1044^\circ\text{K}$ ($k\theta = 0.09$ eV) and $A = 2500$. These are the values of the parameters which were found to give the best fit to the experimental points. The division into two linear parts in a plot of $\alpha^{\frac{1}{2}}$ vs E may be seen most easily from the following formulas:

$$\alpha^{\frac{1}{2}}(\text{abs.}) = \left[\frac{A}{e^{\theta/T} - 1} \right]^{\frac{1}{2}} \Delta E_1,$$

where $\Delta E_1 = h\nu - (E_G - k\theta)$, and

$$\alpha^{\frac{1}{2}}(\text{emiss.}) = \left[\frac{A}{1 - e^{-\theta/T}} \right]^{\frac{1}{2}} \Delta E_2,$$

where $\Delta E_2 = h\nu - (E_G + k\theta)$. The point midway between the intercepts on the energy axis is E_G . When the two α 's are summed, the resultant $\alpha^{\frac{1}{2}}$ is given by the solid curve of Fig. 1.

The constant A determines the ordinate scale and is chosen to fit the absolute experimental values of α . It should be noted that E_G and θ may be determined from measurements of the relative absorption constant. Only A depends on the absolute values of α .

The experimental points of Fig. 1 were obtained by using a p - n junction. At $\alpha^{\frac{1}{2}} = 18$, the points begin to fall below the line because of the nonlinear response for large α . Transmission data do not show this tendency, but their accuracy becomes poor at large α because of the very small transmission. In any case the smaller values of α are sufficient to fit the curves. In extrapolating the upper linear portion to the energy axis, we found at all temperatures an energy difference of about 0.01 eV between results obtained by transmission and by absorption in the junctions. We believe that this is a good estimate of the systematic error due to the nonlinear response of the junctions.

Using the same value of θ but different values of E_G , we were able to fit the experimental data at the three highest temperatures shown in Fig. 2. At lower temperatures we could not fit the complete curve because the phonon absorption part, which depends on the presence of 0.09-eV phonons in the material, becomes very small at low temperatures and falls below the tail of the experimental curve. We therefore assumed that $k\theta$ remained constant at 0.09 eV and from the upper part of the curve we were able to obtain E_G and A . We show

⁵ W. G. Pfann and W. van Roosbroeck, J. Appl. Phys. 25, 1422 (1954).

E_G vs T in Fig. 2. Above 300°K, $dE_G/dT = -3.3 \times 10^{-4}$ ev/degree. At lower temperatures dE_G/dT is numerically smaller, as expected.

The room temperature value of E_G (2.86 ev) agrees with the thermal gap value found from measurements of the forward characteristics of p - n junctions⁶ within the experimental error of those measurements.

We believe that the error in $k\theta$ is not more than 0.01 ev. Adding an uncertainty in the energy intercept of about 0.01 ev, we find a total uncertainty in E_G of about 0.02 ev. Above 300°K our values of E_G are all within 0.005 ev of the straight line shown in Fig. 2.

To calculate A by the formula of Bardeen, Blatt, and Hall requires chiefly a knowledge of the electron-phonon matrix element and of the energy denominator which enters into their second-order perturbation treatment of the problem. The latter is known approximately for materials in which direct transitions are observed. In our case we did not see any sudden increase in absorption rate which might be regarded as the onset of direct transitions. We therefore have only a lower limit for the

⁶ Lyle Patrick (to be published).

energy denominator. Because of the temperature dependence of the energy gaps, we expect some temperature dependence of the energy denominator and hence of A . Experimentally we found that A decreased slowly from about 3500 at 77°K to about 2500 at 717°K.

The electron-phonon matrix element may be estimated from the mobility if it is assumed that the same phonons are involved in both scattering and absorption. This is unlikely, but we have nevertheless used this estimate for want of a better one together with the lower limit for the energy denominator. The value of A calculated in this way is approximately three times as large as our experimental value.

The phonon energy used in fitting the data (0.09 ev) is somewhat less than that of the optical phonons responsible for the strong infrared absorption found by Picus.⁷ We estimate from his curve that these energies are about 0.12 ev for the longitudinal and 0.095 ev for the transverse phonon.

⁷ E. Burstein and P. H. Egli, in *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. VII, p. 24.

Detection of Directional Neutron Damage in Silicon by Means of Ultrasonic Double Refraction Measurements*

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The presence of oriented regions of displaced atoms (directional radiation damage) produced by a beam of approximately collimated fission neutrons in silicon single crystals has been observed by an ultrasonic double refraction method. The effects observed are anisotropic velocity or modulus changes which do not appear to be accompanied by attenuation changes. The irradiated crystal shows a very pronounced ultrasonic double refraction effect with waves propagated at right angles to the bombardment direction together with the absence of such a double refraction effect when the waves are propagated in the direction of the bombarding neutrons. Separate, independent, ultrasonic velocity measurements indicate that the irradiation has lowered the velocities perpendicular to the bombardment direction in a manner entirely consistent with the double refraction measurements. The observed velocity effects are not accompanied by detectable attenuation changes and are therefore not connected with dislocation damping phenomena.

WHEN fast particles such as neutrons collide with atoms in a crystalline substance, the recoiling atom produces what is commonly called radiation damage in the material. The region of damage may be thought of as an elongated ellipsoid, roughly the length of the recoil range, containing many atoms displaced from normal lattice sites. On the average, these elongated regions of damage should be oriented with their long dimension directed along the path of the bombarding particles. Berman, Foster, and Rosenberg¹ have

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¹ Berman, Foster, and Rosenberg, *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 321.

pointed out that the existence of such long thin regions is indicated by their thermal conductivity measurements. Consequently, in a crystal that has been bombarded with a collimated beam to produce a large number of oriented regions, anisotropic physical properties are to be expected. In what follows, anisotropic elastic properties are of particular interest. Such oriented domains of damage will be referred to as directional damage.

An investigation of fast-neutron radiation effects in silicon has shown that it is possible, by means of high-frequency ultrasonic measurements, to observe the effect of directional damage in well-oriented single crystals.