Intrinsic Optical Absorption in Single-Crystal Silicon Carbide

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The optical absorption of single-crystal silicon carbide has been measured in both the cubic and hexagonal, type 6H, modification. The curves nearly coincide for absorption coefficients above 10^3 cm^{-1}. At longer wavelengths the cubic structure absorbs more strongly. The absorption coefficient is 100 cm^{-1} at 2.62 and 3.12 ev, respectively in these two crystals. The electron affinity of silicon carbide is estimated from photo-electric data to be about 4 ev.

INTRODUCTION

SILICON carbide occurs in several crystalline modi-fications.[1] One form is cubic with the ZnS arrange-ment. The others are either hexagonal or rhombohedral and have interatomic distances nearly the same as the cubic. Nearest and next nearest neighbors occupy similar spatial positions in all modifications. Little is known of the band structure of this material, however, and it is difficult to predict the extent of possible differences in the absorption spectrum of these crystals.

Choyke and Patrick[2] measured the optical absorption in the hexagonal modification in the range 10 to 400 cm^{-1} at temperatures from 77 to 717°K. They analyzed their data according to the scheme of Macfarland and Roberts[3] and found that near the threshold of optical absorption the interband transitions are indirect, re-quiring the absorption or emission of a phonon of energy 0.09 ev. The minimum energy separation between valence and conduction bands was found to be 2.86 ev at 300°K. The results presented in this paper are in agreement with their data and extend the curve at room temperature to higher absorption coefficients. In addition, data are given for absorption in the cubic lattice.

EXPERIMENTAL

Single crystals of the hexagonal modification, type 6H, were obtained from the Carborundum Company and J. S. Prener of this Laboratory. Cubic crystals were grown here from the vapor at 1900°C by R. I. Scace and G. A. Slack. Samples were ground to approximate thickness with a diamond saw. Further grinding was accomplished with a fine grade of carborundum and the faces were then polished with aluminum oxide polish-ing powder on a beeswax lap.[4] Absorption measurements were made by the usual sample in, sample out method, correcting for the reflectance. The resolution of the monochromator was about 0.01 ev.

Data were taken parallel to the c axis in the hexagonal crystals. Eight samples, colorless in appearance and ranging in thickness from 8 to 2250 μ were measured. Cubic samples, yellow in color, were more difficult to obtain and only two, 30 and 150 μ in thickness, were available for this study. The magnitude of impurity absorption in these crystals is believed small, however, a contribution from this source to the absorption coeffi-cient below 30 cm^{-1} may be present.

RESULTS

Absorption coefficients for the cubic and hexagonal, type 6H, modifications of silicon carbide at 300°K are plotted in Fig. 1. Above 10^3 cm^{-1} the curves nearly coin-cide. At longer wavelengths the cubic crystal shows the stronger absorption. The coefficient is 100 cm^{-1} at 2.62 and 3.12 ev for the cubic and hexagonal modi-fications, respectively. Absorption in the hexagonal modification agrees quite well with the data of Choyke and Patrick. No break is observed in this curve to indicate the onset of direct transitions.
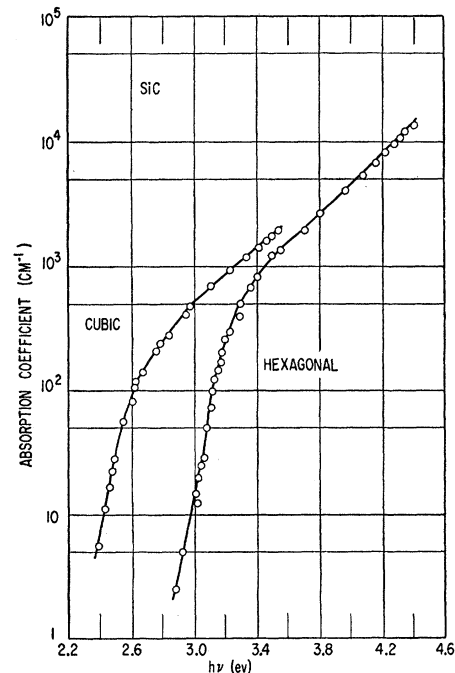

FIG. 1. Absorption spectra of cubic and hexagonal, type 6H, silicon carbide at 300°K.

[1] R. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. 1, p. 23.
[2] W. J. Choyke and L. Patrick, Phys. Rev. **105**, 1721 (1957).
[3] G. G. Macfarland and V. Roberts, Phys. Rev. **97**, 1714 (1955); **98**, 1865 (1955).
[4] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

Not enough is known of the band structure of silicon carbide to predict the extent of changes in the absorption spectrum to be expected. In the region of strong optical absorption the two species appear alike as might be anticipated. Near the threshold of optical absorption, however, the differences are relatively large.[5] If comparison with the band structure of silicon and diamond[6] is significant, then optical transitions in the cubic crystal near the band edge are expected to be indirect.[7] The energy dependence of the absorption coefficient is consistent with this view. It will be of interest to compare the absorption of silicon, cubic silicon carbide, and diamond when absorption coefficients for the latter, obtained over an extended range, are available.

Photoelectric data for cubic silicon carbide are shown in Fig. 2. The threshold of this emission is a measure of the energy difference between the top of the valence band and the vacuum level.[8] This value is slightly greater than 7 ev and comparison with the absorption data indicates that the electron affinity (the energy difference between the bottom of the conduction band and the
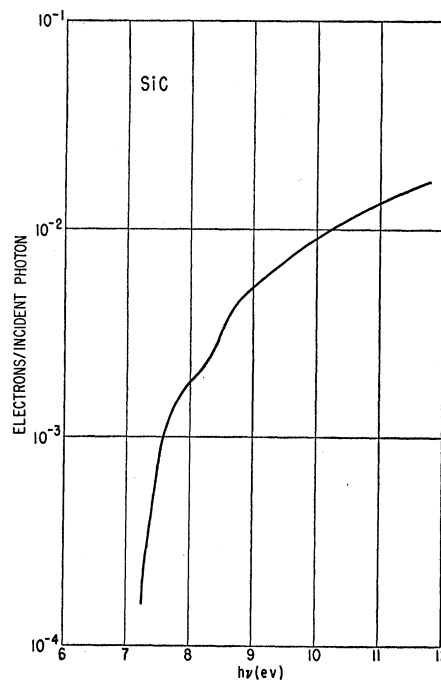

FIG. 2. Spectral distribution of the photoelectric yield for cubic silicon carbide.

vacuum level) is about 4 ev. The band gap of this material is thus comparable to the electron affinity. From a photoelectric point of view this is an interesting situation and is discussed more fully in another place.[9]

[5] Qualitative measurements of optical absorption in cubic and hexagonal ZnS (sphalerite and wurtzite) indicate the threshold of absorption to occur at longer wavelengths in the cubic structure [F. A. Kroeger, Physica 7, 1 (1940)]. This shift of about 0.1 ev at $\sim 10^3$ cm^{-1} is in the same direction as for SiC. No quantitative values for absorption in cubic ZnS have appeared in the literature to afford a more detailed comparison with data on the hexagonal material [W. W. Piper, Phys. Rev. 92, 23 (1953)].

[6] F. Herman, Phys. Rev. 93, 1214 (1954); T. Woodruff, Phys. Rev. 103, 1159 (1956).

[7] 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.

[8] E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids 3, 1 (1957).

[9] Taft, Philipp, and Apker, Phys. Rev. 110, 870 (1958).