Infrared Properties of Cubic Silicon Carbide Films

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Films of cubic silicon carbide have been grown by the reaction of methane with a high-purity silicon surface at 1300°C. Windows of SiC were produced by etching away portions of the silicon. Transmission and reflection measurements in the range 1 to 15 microns have been carefully analyzed according to classical dispersion theory. The dispersion parameters have been determined for the fundamental resonance at 12.60 microns. The dispersion parameters are essentially the same as those for the ordinary ray in the hexagonal α-II form.

I. INTRODUCTION

SILICON carbide is known[1] to occur in a large number of hexagonal and rhombohedral modifications and one cubic modification called the β form. Most of the electrical and optical research reported on silicon carbide has been on the hexagonal α-II form. In all of the forms of SiC each atom of one kind has four nearest neighbors of the other kind at the regular tetrahedral positions. The Si-C distance is always 1.89 A. The cubic β form has the zincblende structure with one SiC molecule per unit cell.

The 12-micron reflectivity band of α-II SiC has been analyzed[2] in terms of classical dispersion theory. The crystals were too thick to permit transmission measurements in the neighborhood of the fundamental absorption band. Recently we have produced thin films of β-SiC of sufficient quality to permit the optical "constants" in the neighborhood of the resonance to be determined from transmission and reflection measurements. Since all of the forms of SiC are very similar, it is reasonable to suppose that the optical constants are very nearly the same. The optical constants deduced from reflectivity studies on the hexagonal α-II form[2] tend to confirm this supposition to a remarkable degree.

This paper describes three phases of the β-SiC investigation: (1) the preparation of the films, (2) the transmission and reflection measurements, and (3) the analysis of the optical measurements in terms of classical dispersion theory.

II. PREPARATION OF THE FILMS

The β-SiC films are produced by heating Si at 1300°C in a mixture of argon and methane. A film of carbon deposits over the Si surface. At the same time a multicrystalline film of β-SiC forms between the Si surface and the C layer. Wherever an SiC film is not desired, its formation can be prevented by an SiO_2 layer on the surface. The essential processing steps for the preparation of the films and the fabrication of the infrared test windows are shown in the flow chart of Fig. 1. The procedure is described in more detail below.

The starting material is a wafer of single-crystal *n*- or *p*-type silicon with approximate dimensions 0.3 by 0.3 by 0.005 inch. The impurity level and the crystal plane of the silicon does not seem to be of importance for the formation of the SiC films. However, the surface appearance of the sample is important since the film becomes an exact replica of the silicon substrate. Therefore, at least one surface is given a good etch finish or mirror polish.

A large number of processing variables can be employed. Films can be formed by heating silicon in either methane or carbon monoxide with or without dilution with argon, helium, nitrogen, or hydrogen. The dilution ratios, times, and the temperatures may be varied over wide limits. On the basis of studies of some of these processing variables, we suggest the following procedure.

The silicon sample is oxidized in O_2 at 1300°C. The resulting SiO_2 layer is removed from the etched or mirror-polished surface with HF. The silicon carbide film is then formed in a furnace which is the same as that employed in the open-tube diffusion process of silicon semiconductor technology.[3] With the furnace at

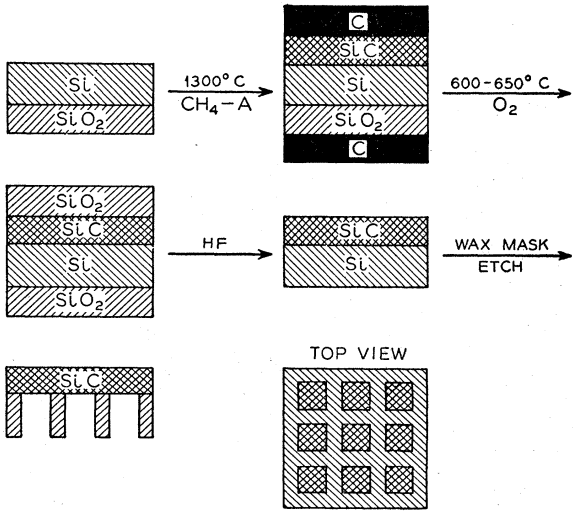

FIG. 1. Diagram indicating the procedure used to produce SiC windows. The dimensions are for exposition and are not significant.

[1] L. Ramsdell, Am. Mineralogist **32**, 64 (1947).
[2] Spitzer, Kleinman, and Walsh, Phys. Rev. **113**, 127 (1959), preceding paper.
[3] C. Frosch and L. Derick, J. Electrochem. Soc. **104**, 547 (1957).

1300°C, argon is passed through the furnace tube at the rate of 1500 cc/minute. Then the silicon sample which is supported in a pusher assembly is quickly inserted into the controlled temperature zone. After a ten-minute preheating period, methane is added to the argon stream at the rate of 6 cc/minute. The sample is allowed to react with the methane for a time which may range from a few minutes to 3.5 hours depending upon the desired thickness of the film. After the heating period, the methane is stopped and the sample is withdrawn at a cooling rate of about 5°C per minute.

When the sample reaches 600–650°C, the withdrawal is stopped. At this temperature the carbon layer may be removed by oxidation without oxidizing the SiC film. The oxidation must be carried on slowly by controlling the amount of oxygen admitted to avoid an excessive temperature rise which can damage the film. After the oxidation, withdrawal of the sample is resumed at the previous rate until the samples reach room temperature. The SiC film forms only on the silicon surface from which the SiO_2 layer has been removed. The samples are now rinsed in HF to remove the SiO_2.

In order to produce windows of SiC supported in a frame of silicon, the silicon surface is suitably masked and sprayed with apiezon wax in trichloroethylene. The samples are then heated above the melting point of the wax to improve adhesion. Finally, the samples are placed in a suitable etch until the unprotected area of the silicon has been etched completely through, thus leaving windows of SiC supported by the remaining silicon.

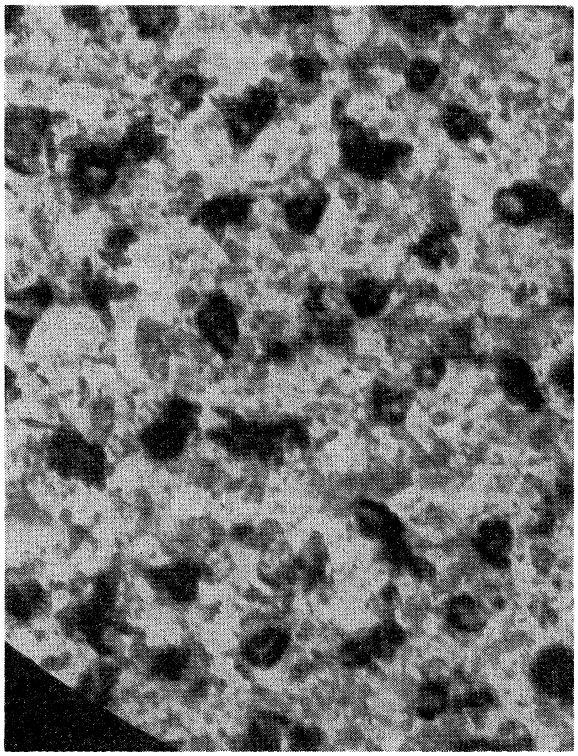

FIG. 2. Electron microscope transmission photograph of a 0.06-μ thick SiC window at 10 000× magnification.

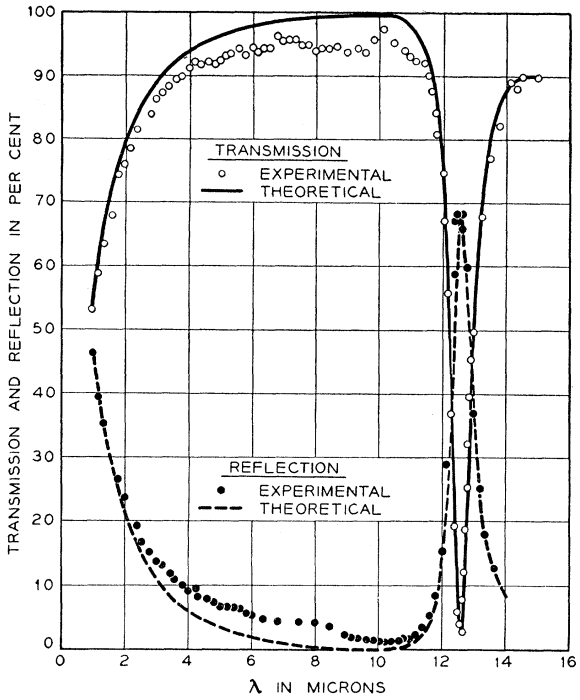

FIG. 3. Transmission and reflection of a 0.06-μ thick window of SiC.

Yields of greater than fifty percent of intact β-SiC windows were consistently produced by this procedure. The films tend to have curved surfaces due to the large difference in thermal expansion between silicon and SiC which places the films under compression on cooling to room temperature. It is believed that this effect would prevent the production of good windows thicker than about 3000 A.

III. EXPERIMENTAL MEASUREMENTS

All measurements were made at room temperature in the wavelength range between 1 and 15 microns with a double-pass Perkin Elmer spectrometer. The sample was placed with the SiC window at a focal point in the exit optical system of the spectrometer, and the infrared beam was confined to an area within the window. The transmission was measured with the conventional sample in-sample out technique, and the reflection by comparing the energy reflected from the sample with that reflected by a good-quality front-surface aluminum mirror.

Electron diffraction examination confirms that the films are polycrystalline and of the β form. An electron microscope transmission photograph is shown in Fig. 2; no holes in the window could be seen at a magnification of 40 000. The thickness of these films was ascertained

on the basis of the optical measurements and the theoretical analysis.

The transmission and reflection for one film as functions of wavelength in microns are shown in Fig. 3. Both the transmission and reflection show the presence of a strong absorption band at 12.6 μ ($\nu_0=2.38\times10^{13}$ sec^{-1}). The region of this absorption is revealed in greater detail in Fig. 4 which shows the transmission for three films of different thickness. Figure 5 shows the reflection for two of the films shown in Fig. 4. In Figs. 4 and 5 the data are represented by points. The curves are theoretical calculations according to classical dispersion theory in which a fit has been obtained to the data by trial and error.

IV. THEORY

The transmission coefficient T and reflection coefficient R' of a uniform film for light at normal incidence are given by[4]

$$T=\frac{L(O)^2+R\sin^2\Psi}{L(\delta)^2+R\sin^2(\alpha+\Psi)}, \tag{1}$$

and

$$R'=R\left[\frac{\sinh^2\delta+\sin^2\alpha}{L(\delta)^2+R\sin^2(\alpha+\Psi)}\right], \tag{2}$$

respectively, where

$$\alpha=2\pi nd/\lambda, \qquad \delta=2\pi kd/\lambda,$$

$$\Psi=\tan^{-1}\left(\frac{2k}{n^2+k^2-1}\right),$$

and

$$L(\delta)=\tfrac{1}{2}[e^{\delta}-Re^{-\delta}].$$

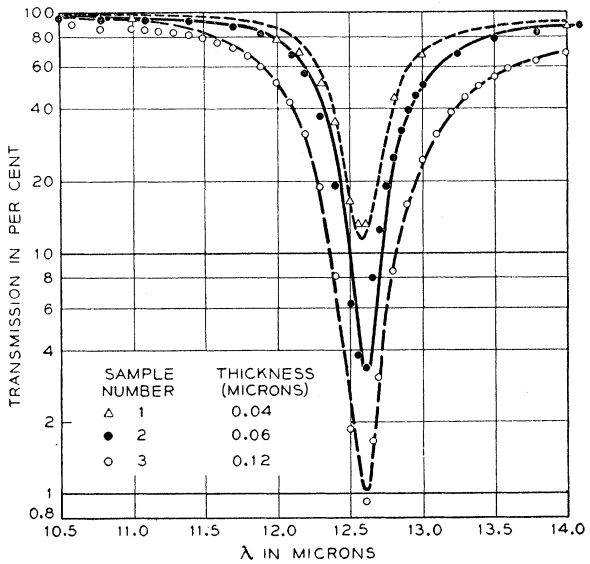

FIG. 4. Transmission of three SiC windows in the spectral region of the resonance absorption band.

[4] B. Barnes and M. Czerny, Phys. Rev. 38, 338 (1931).

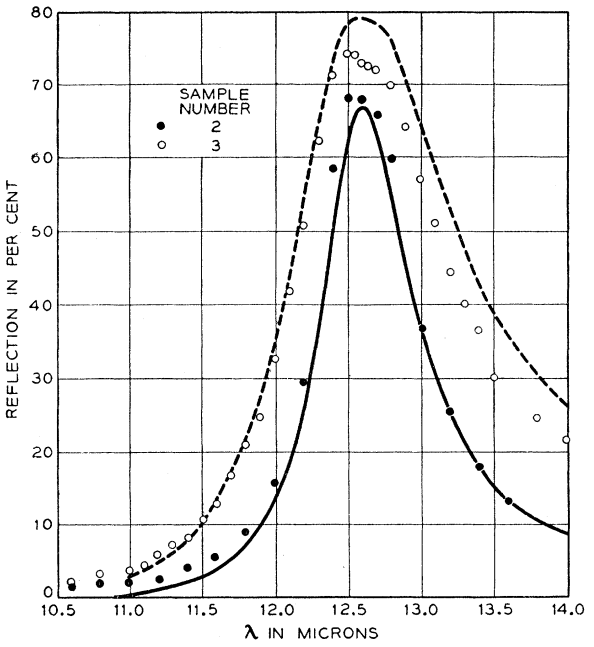

FIG. 5. Reflection of two of the SiC samples of Fig. 4.

The film is characterized by an index of refraction n, an extinction coefficient k, and a thickness d. In the limit of infinite thickness the reflection approaches the reflectivity R, where R is given by

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}. \tag{3}$$

The optical constants n and k could in principle be determined from these equations from measurements of T and R' on a single good quality film of known thickness. The values obtained might be checked against other films of different thickness. However, since the thickness is also an unknown parameter, it becomes impractical to attempt to invert the relations (1) and (2) to obtain the optical constants directly.

We have endeavored to determine the optical constants and at the same time estimate the thickness by expressing n and k according to the classical dispersion theory[2] with four adjustable parameters: ρ, δ, ν_0, and ϵ_0. We seek to find a unique set of values for these four parameters which, through Eqs. (1) and (2), can account for the measured transmission and reflection of several films.

A program was written for the IBM-650 computer to plot n, k, R, R', T as functions of the wavelength λ for any given values of the parameters and the thickness d of the film. The first systematic use of the program was not on the films but on the reflectivity of the α-II hexagonal form of SiC[2]. It was found possible to fit the measured reflectivity within experimental error throughout the fundamental absorption band. The dispersion

parameters determined in this way were then used to compute the expected transmission and reflection of films of various thickness.

V. ANALYSIS AND DISCUSSION

The values of the dispersion parameters used in calculating the theoretical curves shown in Figs. 3, 4, and 5 are

$$\begin{aligned} &\rho=0.263, \\ &\gamma=0.0107, \\ &\nu_0=2.380\times10^{13}\ \text{sec}^{-1}\ (12.60\mu), \\ &\epsilon_0=6.7. \end{aligned} \tag{4}$$

Except for a minor adjustment of γ, these are the same as the values obtained from the reflectivity of α-II SiC. The thicknesses of the various films determined by comparison of theory and experiment is indicated in the figures.

It may be noted that in the immediate region of the resonance the agreement between theory and experiment is very good for both the transmission and reflection. We can not expect similarly good agreement far from the resonance because of other absorption mechanisms such as free carrier absorption neglected in the theory. Indeed, we find that, at the shorter wavelengths, the theory predicts too high a transmission and too low a reflection as seen in Fig. 3. Nevertheless, the qualitative agreement in the range 1 to 10 μ can be considered very satisfactory. Another effect apparent in Fig. 3 is structure between 9 and 10 μ. We find that the quantity $1-T-R'$, which measured the energy loss from the beam, has a small maximum near 9.3 μ which is one of the residual-ray wavelengths of SiO_2.[5] We therefore ascribe the structure to a thin layer of SiO_2 on the surface of the SiC film.

As a check on the method of determining the thickness from the transmission and reflection data, we measured the thickness of one film by an interferometric method. We assume that the film grows both above and below the original silicon surface in accordance with the lattice constants of the two materials. The thickness can then be determined from the step distance between the original surface and the top of the film. This step was produced by masking part of the silicon surface with SiO_2 during the growth of the SiC film. Measurement of the step distance with an interferometer gave for the film thickness 0.14 ± 0.03 μ. Transmission and reflection measurements made on a window in this film 4 mm from the step gave 0.11 μ.

It is of interest that the fundamental lattice absorption frequency of β SiC, $\nu_0=2.38\times10^{13}$ sec^{-1}, is the same as that of the α-II form for the ordinary ray. We find also that the strength of the fundamental absorption measured by $\rho=0.263$ is the same for the two forms. The high-frequency dielectric constant likewise is the same. We find that the absorption width measured by $\gamma=0.0107$ is somewhat greater than the width in the α-II form, $\gamma=0.006$. This may be due to the geometrical form of the thin-film specimens rather than to a difference between the two modifications, or it may be due to differences in the purity of the specimens.

Silicon carbide has a fundamental lattice absorption comparable in strength to those found in the ionic crystals such as alkali halides and magnesium oxide. In those crystals the absorption in the region of the fundamental lattice band has a complicated structure with subsidiary absorptions on the short-wavelength side of the main band. In silicon carbide, however, we have shown that the fundamental lattice absorption can be described by the classical dispersion theory with a single resonance frequency.

ACKNOWLEDGMENTS

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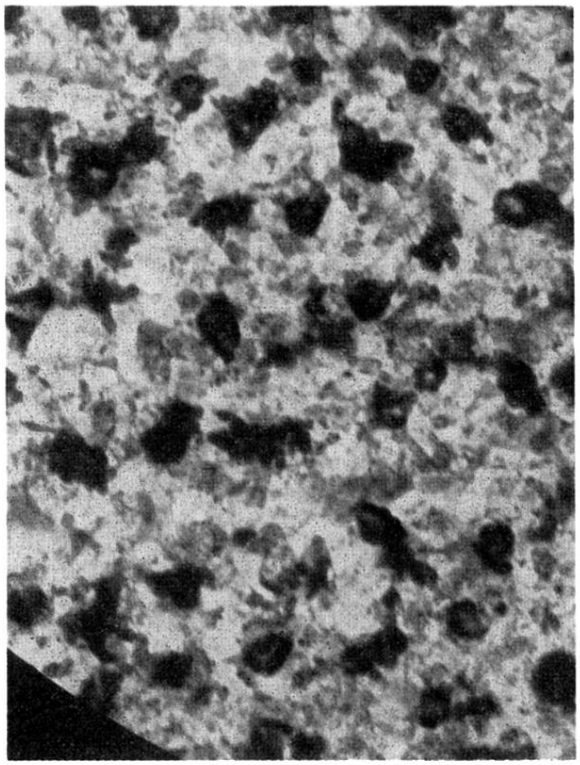
[5] Schaefer, Matossi, and Wirtz, Z. Physik **89**, 210 (1934); F. Matossi and H. Krueger, Z. Physik **99**, 1 (1936).



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