

## Optical constants of cubic boron nitride

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The optical constants of cubic boron nitride were determined for the first time in the vacuum ultraviolet. The fundamental optical-absorption edge determined from these optical constants is  $6.1 \pm 0.2$  eV.

The cubic form of boron nitride (cBN) exhibits various interesting characteristics such as semiconducting properties,<sup>1</sup> high optical band gap,<sup>2-4</sup> extreme hardness, and high melting point. Because of these characteristics, the application of this material to the active devices operating at high temperature will be important in the near future.<sup>1,5</sup> However, the experimental studies relevant to the electronic band structures have not been performed yet, although several theoretical studies on the electronic band structures were already performed.<sup>6-8</sup> Recently, large single crystals of cBN were successfully synthesized by applying the temperature-difference method, which utilizes LiCaBN<sub>2</sub> as a solvent at 55 kbar and 1800 °C.<sup>9</sup> Using these crystals the determination of optical constants of cBN becomes possible and is the purpose of the present study.

Measurements of reflectance and transmittance spectrum were carried out at beam line 1 of SOR-RING (0.38-GeV electron storage ring) of the Institute for Solid State Physics using a 1-m Seya-Namioka-type monochromator in the photon energy range from 2 to 23 eV. Figure

1 shows the reflectance spectrum of a yellow crystal of cBN whose area is nearly 5 mm<sup>2</sup>. Because the top and bottom surfaces of the crystal are not parallel to each other, the reflected light only from the top surface can be detected. Here, incident light is polarized in the plane of incidence and is deflected by 10° from the normal direction with respect to the surface of the crystal. The transmittance spectrum of a 0.16-mm-thick crystal is shown in Fig. 2. Here, light is incident normal to the surface of the crystal. The absolute value of the reflectance and transmittance shown in Figs. 1 and 2 is multiplied by certain factors, respectively, such that the value of the refractive index at a photon energy of 2.10 eV is equal to 2.117, which was determined by Gielisse *et al.*<sup>10</sup> Here, it is assumed from Fig. 2 that the value of the extinction coefficient is zero at this photon energy.

The reflectance and transmittance spectrum shown in Figs. 1 and 2 are used to determine the photon energy dependence of optical constants ( $n, k$ ) in the photon ener-

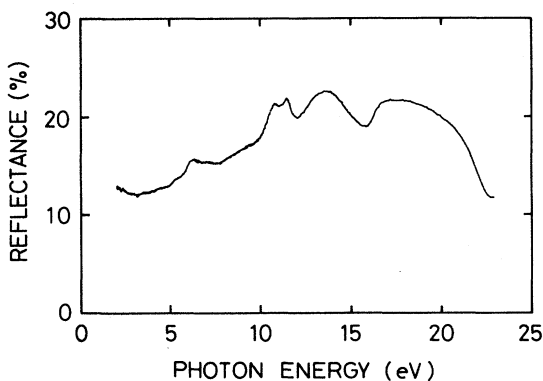


FIG. 1. Reflectance spectrum of cubic boron nitride.

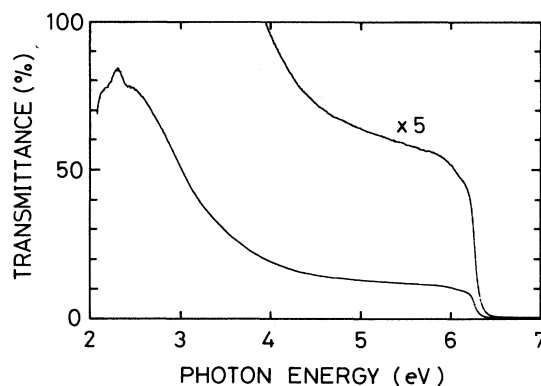


FIG. 2. Transmittance spectrum of 0.16-mm-thick cubic boron nitride.

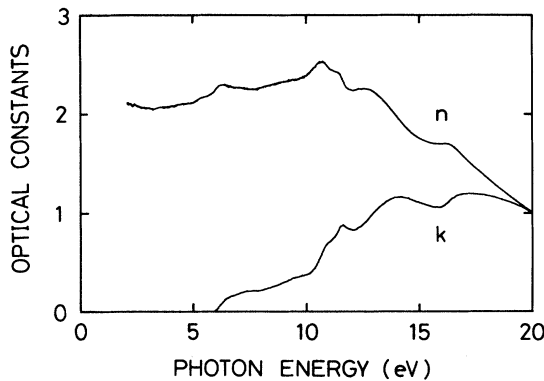


FIG. 3. Photon energy dependence of refractive index  $n$  and extinction coefficient  $k$  of cubic boron nitride.

gy range from 2 to 6 eV using the following expressions:

$$k = \frac{\lambda}{4\pi d} \ln \frac{(1-R)^2}{T}, \quad (1)$$

$$n = \frac{R+1 + [(R+1)^2 - (R-1)^2(1+k^2)]^{1/2}}{1-R}.$$

The optical constants at a higher photon energy are determined from the reflectance and the phase change on the reflection. The phase change on reflection can be

$$\phi(E_i) = -\frac{E_i}{\pi} \int_2^{23} \frac{\ln R(E)}{E_i^2 - E^2} dE + A \ln \left| \frac{2+E_i}{2-E_i} \right| + B \ln \left| \frac{23+E_i}{23-E_i} \right|. \quad (2)$$

Here the values of  $A$  and  $B$  were determined by using a least-mean-squares method so that the values of phase change on reflection are equal to those calculated from the optical constants in the photon energy range from 2.5 to 5.5 eV determined above. If the photon energy approaches 2 or 23 eV, the numerical errors arising from the expression of Eq. (2) increase. Therefore, the phase changes on reflection calculated from Eq. (2) are reliable in the photon energy range from 2.4 to 20 eV. The photon energy dependence of the refractive index and the extinction coefficient thus determined are shown in Fig. 3. The photon energy dependence of the absorption coefficient

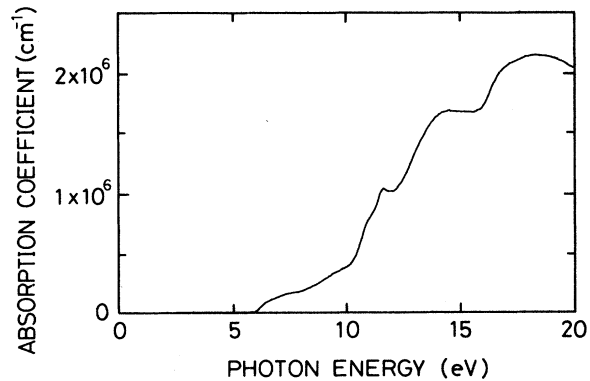


FIG. 4. Photon energy dependence of absorption coefficient of cubic boron nitride.

determined by using the Kramers-Kronig relation which requires the reflectance data in the photon energy range from zero to infinity. Instead of assuming the reflectance data outside the photon energy range in the present measurement, the phase change on reflection is determined by using the generalized mean-value theorem for integrals developed by Roessler<sup>11</sup> in the photon energy ranges from zero to 2 eV and 23 eV to infinity. Namely, the phase change on reflection in the photon energy range from 2 to 23 eV was calculated using the following expression:

calculated from this figure is shown in Fig. 4. According to this figure, the optical absorption of cubic boron nitride is appreciable above the photon energy of  $6.1 \pm 0.2$  eV in addition to the appearance of several absorption edges at higher photon energies.

In conclusion, the optical constants of cubic boron nitride in the vacuum ultraviolet were determined in addition to the determination of the fundamental optical-absorption edge from these optical constants. Further studies will be necessary in order to find the correlation between optical constants and calculated band structures.<sup>6-8</sup>

<sup>1</sup>R. H. Wentorf, Jr., *J. Chem. Phys.* **36**, 1990 (1962).

<sup>2</sup>H. R. Philipp and E. A. Taft, *Phys. Rev.* **127**, 159 (1962).

<sup>3</sup>P. V. A. Fomichev and M. A. Rumsh, *Phys. Chem. Solids* **29**, 1015 (1967).

<sup>4</sup>R. M. Chrenko, *Solid State Commun.* **14**, 511 (1974).

<sup>5</sup>O. Mishima, J. Tanaka, S. Yamaoka, and O. Fukunaga, *Science* **238**, 181 (1987).

<sup>6</sup>A. Zunger and A. J. Freeman, *Phys. Rev. B* **17**, 2030 (1978).

<sup>7</sup>M. Z. Huang and W. Y. Ching, *J. Phys. Chem. Solids* **46**, 977 (1985).

<sup>8</sup>R. M. Wentzcovitch, K. J. Chang, and M. L. Cohen, *Phys. Rev. B* **34**, 1071 (1986), and references therein.

<sup>9</sup>O. Mishima, S. Yamaoka, and O. Fukunaga, *J. Appl. Phys.* **61**, 2822 (1987).

<sup>10</sup>P. J. Gielisse, S. S. Mitra, J. N. Plendl, R. D. Griffis, L. C. Manasur, R. Marshall, and E. A. Pascoe, *Phys. Rev.* **155**, 1039 (1967).

<sup>11</sup>D. M. Roessler, *J. Appl. Phys.* **16**, 1119 (1965); **17**, 1313 (1966).