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Vacuum-ultraviolet reflectance spectra and optical properties of nanoscale wurtzite boron nitride

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The optical reflectance spectra of various wurtzite-BN (w-BN) specimens prepared by the shock-wave method have been measured in the vacuum-ultraviolet region with synchrotron radiation. The optical constants have been determined by applying the Kramers-Kronig relation. The optical band gap was found to be 8.7 ± 0.5 eV, which compares favorably with the latest calculations. The effect of the nanoscale particle size on the reflectance spectra and optical properties is also discussed.

Boron nitride (BN) is a unique ceramic material with extensive applications. It has been indispensable to modern industry and defense. In recent years, the properties of BN have been studied in great detail, both theoretically and experimentally.[1-3] This is mainly due to its fascinating properties, such as extreme hardness, high melting point, low dielectric constant, wide band gap, strong chemical bonding, high resistivity, good heat resistance, etc.

Wurtzite boron nitride (w-BN), space group $P6_3mc$, was first synthesized from hexagonal boron nitride at a static high temperature of approximately 2500 K and high pressure above 11.5 GPa by Bundy and Wentorf[4] in the early 1960s. The following several years saw the shock-wave synthesis method successfully applied, but w-BN remained far from industrialization.[5] There have been thorough and systematic basic studies on cubic-BN (c-BN) and hexagonal-BN (h-BN) up to the present. In contrast, there are many gaps in the experiment researches on the physical and chemical properties of w-BN because of its difficulty in manufacture. No report on w-BN's optical spectra and energy spectra is available. The theoretical calculations on its basic band structure and optical properties[2,3] lack experimental comparison. This paper reports the reflectance spectra of w-BN prepared by the shock-wave method in the synchrotron radiation (SR), vacuum-ultraviolet region. The optical properties are derived; moreover, the changes in reflectance spectra and optical properties of nanoscale w-BN solids heat treated at various temperature are compared.

The samples described in this paper were prepared by the oblique shock-wave method.[6-9] The product was nanoscale w-BN powder. The powder was compacted into a dense solid under isostatic high pressure. Then we shaped samples into thin films for a subsequent 10-h anneal, respectively, at 100 °C and 500 °C, still in the hermetically sealed pipe. Three samples, including the raw nanoscale w-BN powder and two w-BN samples annealed, were selected for powder x-ray diffraction and transmission electron microscopy. The samples were found to be wurtzite-type nanometer microcrystal materials whose particle size increased with the rise of annealing temperature.[10]

The experiments were carried out at the time-resolved spectroscopy station in Hefei National Synchrotron Ra-

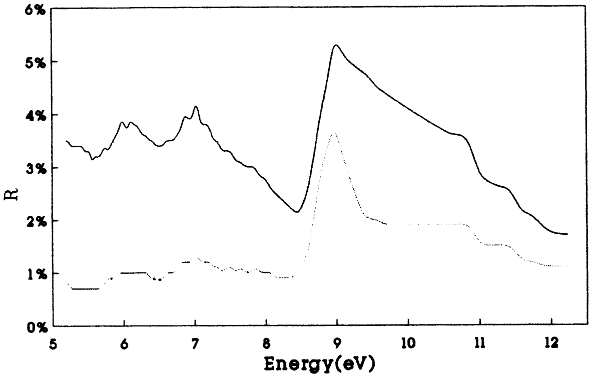

FIG. 1. Reflectance spectra of two samples of *w*-BN (solid line, 500 °C annealed; dashed line, 100 °C annealed).

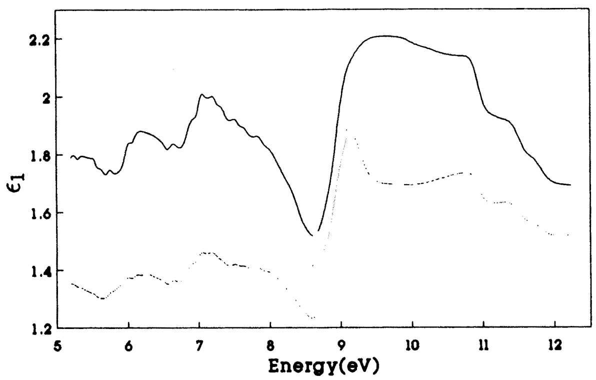

FIG. 3. Spectral dependence of the real part of the dielectric function of two samples of *w*-BN (solid line, 500 °C annealed; dashed line, 100 °C annealed).

diation Laboratory[11] using synchrotron radiation from the 800-MeV storage ring. During the experiment the SR beam current intensity varied within 69–73 mA and the vacuum was kept at 1.5×10^{-6} Pa in the chamber. A standard Au-film sample was put in the chamber together with two samples heat treated at 100 °C and 500 °C, respectively. The integrated reflected intensity i_r was recorded as original data, which were later adjusted for the beam calibration and measuring range calibration. Then $R(\omega)$ is given by

$$R(\omega)=I_R/I_0\ , \tag{1}$$

where I_R is the adjusted reflected intensity from i_r, while I_0, the incident intensity, is calculated from the reflectance of the standard Au film.[12] Thus we have obtained *w*-BN's $R(\omega)$ as shown in Fig. 1.

The complex index of refraction can be determined by $R(\omega)$ and the phase shift $\theta(\omega)$, where $\theta(\omega)$ is given by the Kramers-Kronig relation.[13–17] Stern's method[17] has been used to extrapolate $R(\omega)$ outside the measured energy range of 5.2–12.4 eV. We have used the method to calculate optical constants of CdS, which turned out fully consistent with experiment.[14] Then, we can obtain all the optical properties of nanoscale *w*-BN materials from their reflectance spectra. The absorption coefficient ($\alpha=4\pi\kappa/\lambda$), the real part of dielectric function (ϵ_1), and the imaginary part of dielectric function (ϵ_2) of the two samples are shown in Figs. 2, 3, and 4, respectively.

Figure 1 shows the two samples' reflectance spectra to be similar in shape and position. The main feature at about 9.0 eV describes the interband transition of *w*-BN and indicates it to be a wide band-gap material. In Fig. 2, it can be found that the absorption coefficient rapidly rises to maximum within the range 8.5–9.0 eV for both samples. The absorption edge indicates the onset of strong direct transitions, which leads us to the conclusion that *w*-BN has an optical band gap of 8.7±0.5 eV. This is the first experimental result on an optical band gap of *w*-BN and is basically consistent with the latest calculation of 8.0 eV about direct transition at the Γ point.[2]

Owing to interface relaxation and grain growth, the sample annealed at 500 °C is closer to perfect crystal than 100 °C. As a result, the reflectivity improves considerably, compared with that of the *w*-BN sample annealed at 100 °C. All optical properties as shown in Figs. 2–4 are quite similar. The nanoscale *w*-BN with apparent crystal structure is not only different from noncrystalline solids, but also different from perfect crystalline solids because of a large amount of disordered components in interfaces.

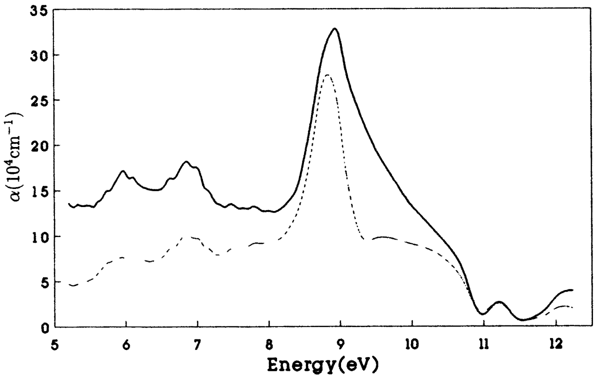

FIG. 2. Spectral dependence of the absorption coefficient of two samples of *w*-BN (solid line, 500 °C annealed; dashed line, 100 °C annealed).

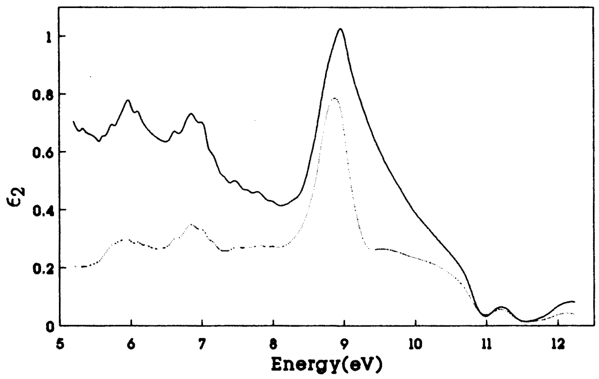

FIG. 4. Spectral dependence of the imaginary part of the dielectric function of two samples of *w*-BN (solid line, 500 °C annealed; dashed line, 100 °C annealed).

The discernible difference on optical properties between nanoscale *w*-BN annealed at 100 °C and 500 °C may show transition from nanoscale structure to bulk crystals.

This paper reports the VUV reflectance spectra of nanoscale *w*-BN and estimates the band gap at 8.7±0.5 eV from spectral dependence of optical properties. The optical properties of the nanoscale state and ordinary bulk structure are compared, which may be instructive for future studies. Further studies will be necessary in order to find the correlation between optical constants and calculated band structure.

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