Indirect Band Gap of Light-Emitting BC_2N

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(Received 2 June 1999)

We have employed high resolution electron energy loss spectroscopy (HREELS) (in ultrahigh vacuum) to investigate the band gap of the novel semiconductor BC_2N by measuring electronic excitations from the valence band to the conduction band. Angle-resolved HREELS allows the observation of transitions which are not vertical in k space, and the measurements indicate an indirect band structure, even though this material emits visible photoluminescence. The results also reconcile scanning tunneling microscopy and photoluminescence measurements for the system.

PACS numbers: 73.61.Le, 78.55.–m, 79.20.Kz

The new BC_xN compounds [1–7] are expected to behave as semiconductors with a "tunable" band gap energy which can be controlled by their atomic composition. They are layered materials based on an atomic scale mixture of graphite, which is a semimetal [8], and boron nitride (BN), an insulator with a band gap of 6 eV. Recent research includes both experimental [1–7,9,10] and theoretical [11–18] studies and also extends from the layered BC_xN compounds to semiconducting nanotube structures [1–4,11–13].

Thin films of BC_2N, which is a particularly reliable composition of the BC_xN compounds, are found to be p-type semiconductors [5,6]. They represent an atomic level hybrid of the B, C, and N atoms, rather than a mixture of C and BN phases [7,19]. BC_2N also has optical properties which are of special interest. Photoluminescence (PL) from BC_2N, with peak intensity at wavelengths of 580–600 nm, has been reported recently [5]. The PL was observed at both 4.2 K and at room temperature, with external quantum efficiencies of $>1\%$ and $>0.5\%$, respectively. This suggests the possibility of BC_2N based light-emitting devices, and would normally indicate that the material has a direct band gap. However, the inferred band gap from the PL measurement of 2.1 eV [5] is not in total agreement with spectroscopic scanning tunneling microscopy (STM) results [5], which indicate a lower band gap (perhaps around 1.4 eV). Thus the nature of the band structure of BC_2N (in particular, whether the material has a direct or indirect gap) is one which needs to be resolved.

In this Letter the band structure of BC_2N is addressed using high resolution electron energy loss spectroscopy (HREELS) in ultrahigh vacuum (UHV). HREELS measures the electronic excitations from the valence band to the conduction band. Angle-resolved HREELS allows the observation of both vertical (optical) transitions and transitions which are not vertical in k space. Measurements of the (apparent) band gap as a function of k show a negative dispersion, which indicates an indirect band structure. This observation is compared with theoretical calculations [15] and reconciles the band gap which can be inferred from scanning tunneling microscopy results for the system with the (vertical) gap obtained from photoluminescence spectra [5].

The BC_2N thin films used in this study were prepared by the chemical vapor deposition method using boron trichloride (BCl_3) and acetonitride (CH_3CN) [20,21]. The substrate was a piece of cleaved highly oriented pyrolytic graphite, which was held at about 850 °C during deposition. The film thickness was about 1 μm, as determined from the depth profile in secondary ion mass spectrometry measurements. The average atomic percentages of boron, carbon, and nitrogen, determined by x-ray photoelectron spectroscopy, were 25%, 56%, and 19%, respectively, showing a composition close to that of BC_2N [5]. The HREELS measurements were conducted in a UHV chamber with a base pressure of 3×10^{-10} torr. Sample heating was performed by electron bombardment of the back of the substrate and the sample temperature was measured using an infrared pyrometer. The sample was flashed to about 800 °C to clean the surface before HREELS measurements. The angle-resolved HREELS measurements employed an LK3000 spectrometer, with incident electron beam energy of 20 eV and an energy resolution set to 10–15 meV to increase the signal levels.

Figure 1(a) shows a series of HREELS spectra recorded with different electron scattering geometries. All spectra

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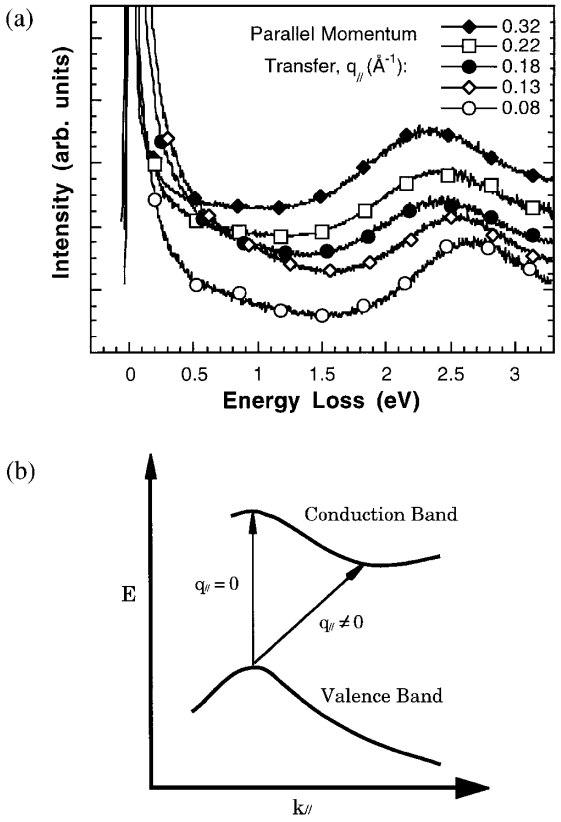

FIG. 1. (a) HREELS spectra from a thin film of BC_2N for different parallel momentum transfer. The broad loss features observed above a threshold at 1–2 eV are due to interband transitions. (b) Schematic illustration of two interband transitions with $q_\parallel = 0$ (vertical) and $q_\parallel \neq 0$.

show a strong elastic peak, followed by a flat and featureless region and then a broad energy loss peak. This energy loss peak is attributed to interband transitions from the valence band to the conduction band. The onset of the energy loss peak in the spectrum gives the energy gap corresponding to that particular scattering geometry. Conservation of momentum parallel to the surface uniquely identifies the wave vector of the interband transitions, $q_\parallel$, according to

$$q_\parallel = k_{i\parallel} - k_{s\parallel}\,, \tag{1}$$

where $k_{i\parallel}$ and $k_{s\parallel}$ are the components of the wave vector of the incident and scattered electron parallel to the surface. $q_\parallel$ depends on both the exit angle and energy loss through the kinematic relations

$$E_{\text{loss}} = E_i - E_s\,, \tag{2}$$

$$q_\parallel = \frac{\sqrt{2mE_i}}{\hbar}\left(\sin\theta_i - \sqrt{1 - \frac{E_{\text{loss}}}{E_i}}\,\sin\theta_s\right), \tag{3}$$

where E_i and E_s are the energies of the incident and scattered electron, while θ_i and θ_s are the angles of the incident and scattered electron beam with respect to the surface normal.

The threshold, then, of the energy loss peak in the HREELS spectrum is the transition within the band structure, with well-defined $q_\parallel$, at which one finds a minimum energy difference between the valence band and the conduction band. The key result which emerges from Fig. 1(a) is that the observed energy gap decreases with an increase in parallel momentum transfer ($q_\parallel$). This effect is illustrated schematically in Fig. 1(b), where two transitions, with $q_\parallel = 0$ and $q_\parallel \neq 0$, are shown within a schematic band structure. Note that the schematic diagram assumes that the valence band maximum lies at the Brillouin zone center, as calculated theoretically by Liu *et al.* [15], but that this assignment is not required to conclude from the HREELS measurements that the gap is indirect.

The decrease in the threshold energy with increasing $q_\parallel$ in Fig. 1(a) is indicative of an indirect band structure (a direct gap band structure would show a minimum in energy gap for $q_\parallel = 0$). Plotting the experimental energy gaps [from Fig. 1(a)] as a function of $q_\parallel$, Fig. 2, shows this effect clearly, with the largest band gap (1.8 ± 0.1 eV) measured at small $q_\parallel$. It was not possible to measure at exactly $q_\parallel = 0$, due to experimental constraints on the scattering geometry. The data in Fig. 2 were extracted quantitatively from HREELS spectra by fitting the loss peaks to Gaussian profiles, after subtraction of a smoothly varying background, and taking the onset to be where the loss intensity is 10% of the peak loss intensity. This method gives a reliable, nonsubjective measure of the onset. The error bars marked in Fig. 2 are estimated from the reliability of the fitting procedure.

To compare our results with previous experimental observations, Fig. 2 also summarizes the results of PL and

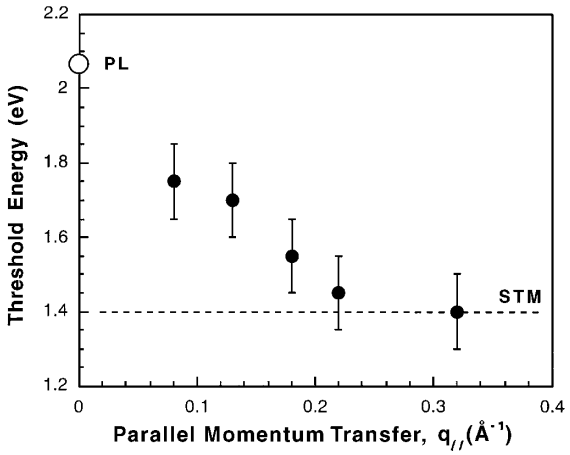

FIG. 2. Threshold energies of the interband transitions for BC_2N thin films as a function of parallel momentum transfer. Also shown is the vertical band gap derived from PL measurements (open circle at $q_\parallel = 0$) and that indicated by STM measurements, where $q_\parallel$ is not conserved (horizontal line) [5].

spectroscopic STM measurements [5]. The PL spectra show a peak at 2.1 eV at room temperature, suggesting a band gap of 2.1 eV (taken to be at the Brillouin zone center, as discussed above), which is marked with a circle in Fig. 2. Spectroscopic (i.e., I-V) measurements with the STM reflect the density of electronic states (without reference to $q_{\parallel}$). The STM energy gap of about 1.4 eV is different from the PL gap. However, the negative dispersion of the band gap implied by our HREELS observations harmonizes the PL and STM measurements in terms of an indirect band picture. Specifically, the HREELS measurements approach the PL result for the vertical gap at low $q_{\parallel}$, Fig. 2, while STM integrates the density of states across a wide range of $q_{\parallel}$. Given the indirect band structure, one would expect the STM gap to be smaller than the vertical gap obtained from PL, as observed. Thus the HREELS measurements which (to our knowledge) provide the first experimental indication that BC_2N has an indirect band structure, also reconcile the previously reported PL and STM results.

The experimental results can be compared with theoretical investigations of the band gap of BC_2N. The band gap is predicted to be highly dependent on the atomic arrangement and crystallinity [15–18,22]. Experimental information on the atomic arrangement is limited, although several theoretical treatments have been conducted [15–18]. For example, Liu *et al.* [15] have calculated several possible atomic arrangements in the BC_2N monolayer together with the associated band structures, using the pseudopotential local-orbital approach. The calculated band structures indicated that two of the structural models for BC_2N would be semiconductors with indirect band gaps of 1.6 or 0.5 eV, while a third possible structure would be a metal. The most stable of these predicted atomic structures of the BC_2N sheet includes zigzag chains of C-C and B-N atoms and has an indirect band gap of 1.6 eV. The experimental observations reported here thus agree with Liu *et al.*'s prediction of an indirect band gap [15].

In summary, we have employed HREELS in UHV to investigate the band gap of BC_2N by measuring the electronic excitation spectrum from the valence band to the conduction band as a function of parallel momentum transfer. The excitation threshold (apparent gap) shows a negative dispersion, which indicates an indirect band structure. This observation is consistent with theoretical calculations and harmonizes scanning tunneling spectroscopy results for the system with photoluminescence spectra. This finding could also have important consequences for the use of BC_2N in fast optoelectronic devices. In future, experimental studies which combine UHV HREELS measurements with *in situ* STM measurements may be expected to make an important contribution to the elucidation of the electronic properties of novel materials such as BC_2N.

Y. C. acknowledges financial support from the University of Birmingham and the ORS committee.

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