Observation of near-band-gap luminescence from boron nitride films

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We report results from cathodoluminescence spectroscopy of boron nitride films grown on Si(100) substrates by ion-source-assisted magnetron sputtering of a hexagonal BN target. Three main peaks are observed in the near-band-gap region for hexagonal boron nitride films at energies of 4.90, 5.31, and 5.50 eV. We also report deep-level emission spectra of predominantly cubic boron nitride films which are correlated with sample growth conditions. In particular we show that the emission intensity, position, and linewidth are strongly dependent on the substrate bias voltage used during sample growth.

The development of III-V nitride materials is of considerable interest for semiconductor electronic and optical device applications.[1] The band gaps of III-V nitrides range from 1.9 eV for wurtzitic InN to greater than 6.2 eV for cubic BN, making these materials well suited for optical applications throughout the visible and into the near-UV region. Recently, we presented evidence of a low energy (on the order of 100 eV) kinetic threshold in the growth of cubic BN films on Si(100) substrates by magnetron sputtering.[2] Using this deposition technique, we have grown, depending on growth conditions, both high quality hexagonal BN films and predominantly cubic BN films on Si(100) substrates.

Although the polytypes of boron nitride have some of the largest band gaps of the III-V nitrides and are technologically important materials for deep-blue and UV applications, their luminescence properties are not well characterized. While several researchers have reported unidentified defect- and impurity-related deep-level luminescence from both hexagonal and cubic boron nitride,[3-8] there has been only one report of luminescence at wavelengths near the band edge in this compound, namely the work of Lukomskii *et al.*,[9] which was performed with single-crystal hexagonal BN. The apparent absence of near-band-gap luminescence properties of BN compounds from the literature may be attributed to the lack of high quality, low defect-density samples necessary for quantitative study. Typically both bulk crystal and thin film samples of the BN polytypes contain a high density of stacking faults, nitrogen vacancies, high impurity concentrations, and often mixed phases. This is reflected in the large range of reported band gaps for both hexagonal[9-12] and cubic[13-16] BN. In this letter, we report the first observations of near-band-gap luminescence from hexagonal boron nitride films and also discuss correlations between growth conditions and selected spectral features of cubic boron nitride films.

Boron nitride films were grown on Si(100) substrates by an rf magnetron sputter deposition process. During growth, the substrates were biased negatively with respect to ground and were immersed in a nitrogen plasma produced by an electron cyclotron resonance source. Our previous work determined the existence of a sharp threshold in the substrate bias voltage beyond which cubic BN is formed.[2] The growth process was studied in detail using reflection high energy electron diffraction (RHEED). The threshold, which occurs at bias voltages on the order of −100 V, is revealed by distinct differences in the RHEED ring patterns of hexagonal and cubic BN. Further, the structural quality of the cubic BN films, as monitored by the ring width of the RHEED patterns, is found to be optimized in a very narrow window of voltages just beyond the threshold.

Cathodoluminescence (CL) measurements were performed in an ultrahigh vacuum (UHV) chamber at a base pressure of 5×10^{-10} Torr. Samples were mounted with either indium or silver paint on a UHV compatible open-flow liquid helium cryostat capable of temperature control from 4.2 to 400 K. Sample temperature was monitored with a silicon diode and controlled to within 0.5 K using a Lakeshore 91C temperature controller. The CL was excited with a Vieetech VE-052 electron gun operated at an acceleration voltage of 30 keV and a filament current of 60 μA producing a beam current at the sample of ~3.0 μA. The spot size at the sample was maintained at 2 mm or larger to reduce effects of sample heating. The CL was focused onto the slits of an ISA THR1000 spectrometer equipped with a grating blazed at 250 nm. The spectrometer was operated in first order with a spectral resolution of 0.02 eV. A UV sensitive photomultiplier tube (RCA C31034a-02) operating in photon-counting mode was used to detect the CL signal. Spectra were not corrected for instrumental response.

A hexagonal BN film, of ~8000 Å thickness, was grown at 850 °C without substrate bias and was characterized by IR absorption measurements and high resolution transmission electron microscopy (HRTEM). The film is characterized by strong IR absorptions at 788 and 1383 cm^{-1} from hexagonal BN TO phonons.[11] In this film, there is no evidence of sp^3 bonding, which would generate a feature near 1065 cm^{-1} corresponding to the cubic BN TO phonon absorption.[17] HRTEM confirmed that this film is highly oriented hexagonal BN, with the hexagonal BN (002) planes aligned perpendicular to the silicon substrate surface. This highly oriented growth mode of hexagonal BN on silicon (100) substrates has been observed previously.[18]

The low temperature CL spectrum of this hexagonal BN film, shown in Fig. 1(a), is dominated by three deep-level emission bands centered at 3.40, 3.84, and 4.40 eV. In addition, three near-band-gap UV emission peaks centered at energies of 4.90, 5.31, and 5.50 eV are observed [Fig. 1(b)]. To our knowledge, these near-band-gap features have not been reported previously in any type of boron nitride film. Recent CL studies of single crystals of hexagonal BN showed similar UV luminescence features, as well as additional features
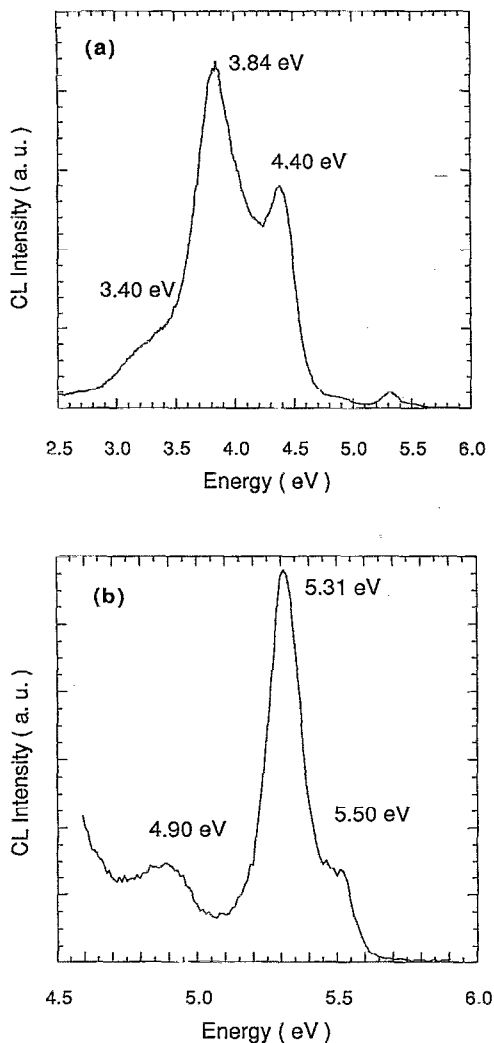
FIG. 1. (a) Deep-level and (b) near-band-gap UV emission spectra measured at 4.2 K on a hexagonal BN film.

FIG. 2. Temperature-dependent CL spectra from a hexagonal BN film in the near-band-gap region.

tivation energy, E_a, of 37 ± 5 meV. We consider this to be a lower bound since localized beam heating of the sample has not been taken into account. Also apparent in the data is that the peak positions are not strongly temperature dependent, which is consistent with both experimental measurements and theoretical expectations of the band-gap temperature dependence of hexagonal BN.[12] The measured shift of the hexagonal BN band gap with temperature is lower by at least an order of magnitude compared to shifts in cubic III-V materials.

We have also examined the deep-level emission from a series of 2000-Å-thick polycrystalline cubic BN films grown with varying substrate bias. These cubic BN films were grown under identical conditions except for substrate bias

at energies as high as 5.8 eV.[9] The widths of the UV emission lines from our hexagonal BN film are approximately a factor of 2 greater than those reported for single-crystal BN. We attribute the increased linewidth to inhomogeneous broadening due to the small-grain polycrystalline nature of the film. Similar broadening has been observed, for example, in the near-band-gap emission from polycrystalline diamond films.[19,20] We also point out that the energy separation between the two highest energy peaks is 199 meV, close to the reported value of the hexagonal BN in-plane LO phonon energy ($\hbar\omega_{LO}=199.6$ meV),[21] which suggests a phonon-assisted radiative recombination process. The exact origin of the observed peaks is currently under investigation.

The temperature dependence of the near-band-gap CL features is shown in Fig. 2. As can be seen in Fig. 2, the intensities of the peaks decrease rapidly with increasing temperature above 60 K and yet, all features are still resolvable at 250 K. The temperature-dependent integrated intensity of the highest energy peak (5.50 eV) was fit to the expression $I(0)/[1+C \exp(-E_a/kT)]$, giving a lower bound on the ac-
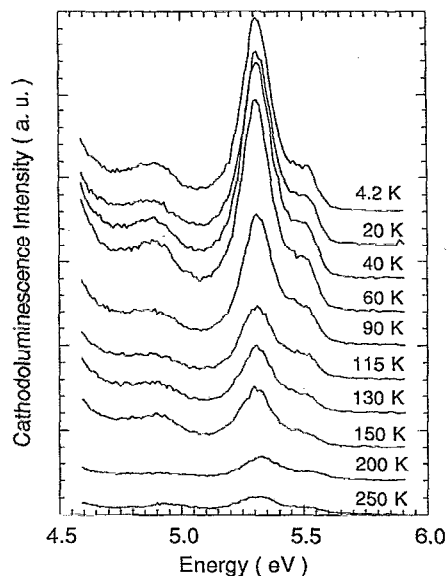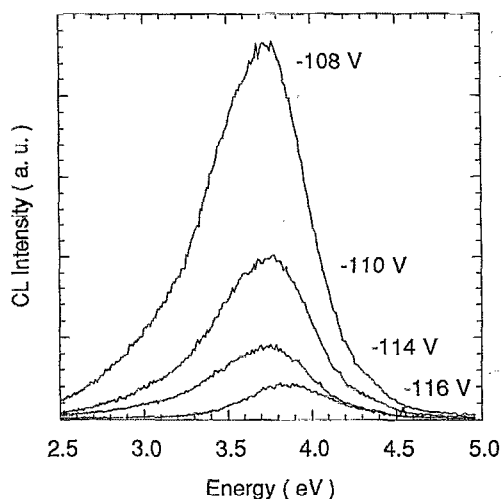

FIG. 3. Deep-level emission spectra of predominantly cubic BN films grown at substrate bias voltages ranging from -108 to -116 V.
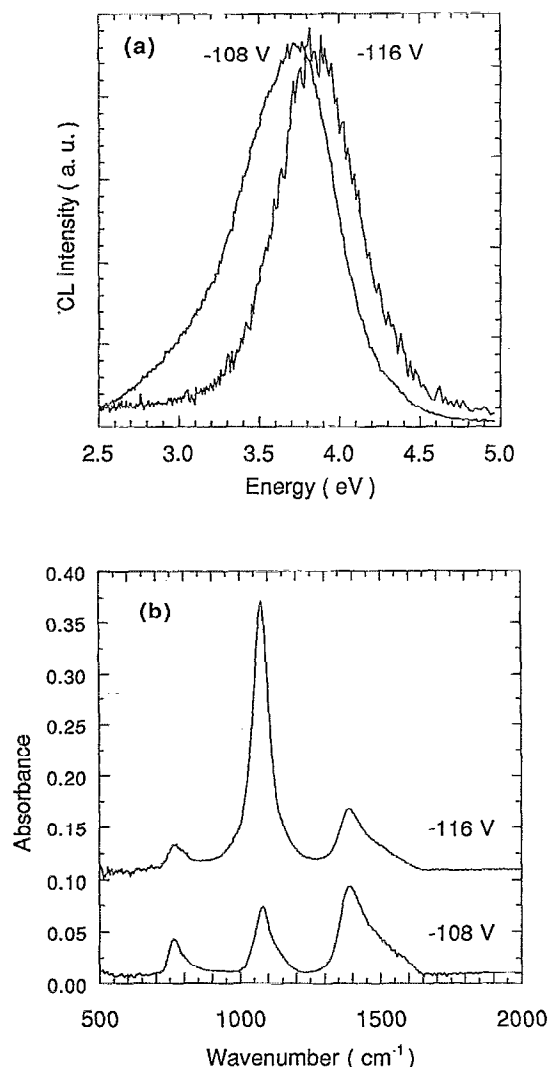
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FIG. 4. (a) Normalized CL spectra and (b) IR absorption spectra of predominantly cubic BN films grown with substrate bias voltages of -108 and -116 V. The IR absorption near 1065 cm^{-1} corresponds to the cubic BN TO mode and the small absorptions near 780 and 1380 cm^{-1} are from the thin layer of hexagonal BN near the substrate.

crease in absorbance at 1065 cm^{-1} reflects the improved crystallinity of the cubic BN film grown with a substrate bias of -116 V. It is expected, as we extend our research to study near-band-gap emission from cubic BN films, that an inverse relationship will be observed between deep-level and near-band-gap luminescence features as the crystallinity of the cubic BN films is optimized. Similar findings have been reported for vapor deposited diamond films in which the free exciton emission/band A emission is strongly correlated with growth conditions.[22]

In summary, we have presented the first near-band-gap UV emission from a hexagonal BN film. Three main peaks were observed in the UV emission spectrum at energies of 4.90, 5.31, and 5.50 eV. We also examined cubic BN films and found strong correlations in the intensity, linewidth, and position of defect-related visible emission with substrate bias voltage used during growth. In particular, the defect-related emission was found to decrease in intensity and shift to higher energy as the cubic BN growth conditions were optimized. We are currently investigating the origin of the near-band-gap emission from hexagonal BN films and extending our research to examine near-band-gap emission from cubic BN.

voltage which was varied systematically from -108 to -116 V. This range of substrate bias voltage is just beyond the threshold value for cubic BN formation with our current growth conditions, which results in optimization of the cubic BN crystalline quality near -116 V.[2] HRTEM measurements confirmed that the films have a thin amorphous layer adjacent to the silicon substrate followed by an ~ 200 Å hexagonal BN layer with the remainder of the film being cubic BN. A thin amorphous layer has been reported previously for cubic BN films on silicon (100) substrates.[18]

The deep-level defect-related CL, shown in Fig. 3, diminishes significantly in samples grown with increasing substrate bias voltage. Normalized CL spectra for samples grown at -108 and -116 V, shown in Fig. 4(a), demonstrate that, in addition to the decrease in intensity, the emission linewidth narrows substantially and shifts to higher energy as the cubic BN crystal quality is optimized. The IR absorbance of the two samples is shown in Fig. 4(b). The relative in-

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