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Luminescence properties of hexagonal boron nitride: Cathodoluminescence and photoluminescence spectroscopy measurements

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Cathodoluminescence and photoluminescence spectroscopies have been performed on hexagonal boron nitride powders. The combination of these techniques allows us to analyze the two observed luminescence bands. A deep-level UV emission at about 4 eV is attributed to defects or impurities, and a near-band-gap UV emission is observed at about 5.5 eV. The deep-level band is composed of four peaks, which are attributed to phonon replica due to localized vibrations. In the near-band-gap region, six components are observed between 5.2 and 5.96 eV, in agreement with the recent experiments performed on h-BN single crystals by Watanabe *et al.* [Nat. Mater. **3**, 404 (2004)], but they are assigned here to Frenkel excitons.

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I. INTRODUCTION

Hexagonal boron nitride (h-BN) is a wide-band-gap semiconductor (estimated at about 6 eV) and, therefore, a promising material for optoelectronic applications, including UV light emitters.[1] Its development has been limited because of synthesis difficulties but the interest in this compound has been considerably renewed recently with, in particular, the discovery of BN nanotubes consisting in rolled up h-BN sheets.[2,3] Sophisticated electronic structure and optical spectrum calculations concerning h-BN[4,5] as well as BN nanotubes have then been undertaken.[6,7] As usual, it has been found that the band gap calculated within the standard density-functional theory–local-density approximation (DFT-LDA) scheme is strongly underestimated, while the indirect band gap increases from about 4 eV to much higher values in the range of 5.4–6 eV when are included the so-called GW quasiparticle corrections.[5,8] Surprisingly enough, huge excitonic effects have also been found in the optical spectra so that the final prediction[5] is that the lowest excitonic state lies at 5.85 eV with a strong binding energy (in reference to the direct band gap) of 0.72 eV. This shows that we are dealing with fairly localized Frenkel-like excitons, and not with Wannier excitons. These confinement effects are predicted to be still much larger in nanotubes[6,7] and seem to have been observed in absorption spectroscopy experiments.[9] The conclusion of these theoretical studies is that, although experimental values for the optical gap about 6 eV have already been reported, the interpretation of the spectra in terms of single-particle interband transitions should be replaced by interpretations in terms of Frenkel excitons.

On the experimental side, because of the lack of large pure samples, the electronic and optical properties of hexagonal boron nitride remain relatively unknown until now. Some photoluminescence (PL) experimental studies have shown a broad signal attributed to a direct and an indirect band gap located around 4 eV,[10,11] which is not very plausible, according to the recent theoretical analyses presented above. In the meantime, cathodoluminescence (CL) spectroscopy has demonstrated the existence of near-band-gap structures in the UV range.[1,12,13] The more precise data are certainly those by Watanabe *et al.*,[1] thanks to the quality of their samples. These authors claim to have measured a direct band gap at 5.975 eV and proposed that excitonic effects were at the origin of a high luminescence peak observed at 5.765 eV (215 nm). They assigned this phenomenon to a free Wannier exciton with a 0.149 eV binding energy, but as mentioned above, the theoretical analysis presented by Arnaud *et al.*[5] disagrees with this interpretation.

Clearly, further work is required to elucidate the precise nature of the optical spectra. Because spectroscopic details are frequently dependent on the techniques used, it is also desirable to combine CL and PL data. The advantage of PL, which uses an optical (laser) excitation is its frequency selectivity which can, for instance, be used to look for resonance effects. On the other hand, CL has the advantage in our case of permitting fairly easy investigations in the far UV, the excitation being provided by electrons of a few tens of keV. It can also be combined with electron microscopy images which are very useful when studying small objects.

In this paper, we present such a study and perform a detailed analysis of two luminescence bands at about 4 and 5.5 eV. The main result is that, while the structures at high energy are attributed to excitons, the blue band at 4 eV is attributed to generic defects (carbon or oxygen impurities, vacancies) of the structure and not to the optical gap, as has been frequently made in the literature (see, e.g., Ref. 10, and references therein).

II. EXPERIMENTAL DETAILS

High-quality commercial h-BN powders (Aldrich Corp.), with less than 2 wt. % of impurities, have been analyzed. The main impurity is known to be boron oxide and/or boric acid (which is easily dissolved, for example, in ethanol). X-ray diffraction shows crystallite sizes of 200 nm in the basal plane and 90 nm in the other direction. Powders with smaller crystallite sizes,[14] about 20–50 nm in the basal plane, have also been used to check that the observed spectra do not vary significantly with this size. Different techniques have been used to look for the presence of impurities: x-ray photoelectron spectroscopy (XPS) has revealed the presence of carbon and oxygen but electron-energy-loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDX) have not revealed significant amounts of impurities, in particular, after the preparation processes described below.

PL spectroscopy is carried out in a backscattering configuration with the sample placed in a cryostat (ST-100 Janis Research Co.), allowing the temperature to be lowered from 298 to 4 K. The samples are prepared by depositing on suprasil slabs crushed powders or droplets of h-BN suspensions in ethanol. The PL spectra are recorded using frequency-quadrupled (266 nm, i.e., 4.66 eV) and frequency-quintupled (213 nm, i.e., 5.82 eV) Nd:YAG (yttrium aluminum garnet) laser with a pulse duration of 10 ns. The laser beam is focused on the sample down to a 200 μm spot diameter. The emitted spectra are dispersed with a single-grating monochromator (1200 grooves/mm, H20 UV, Horiba Jobin-Yvon SAS), amplified by a photomultiplier (R955, Hamamatsu), and detected by a fast numerical oscilloscope (TDS3052, Tektronix). The resolution of the setup is 1.5 nm.

High-resolution PL measurements have also been performed using a highly dispersive spectrograph (Acton Insight 400B) equipped with two gratings (300 and 2400 grooves/mm) and a charge-coupled device (CCD) camera (400 × 1340 pixels, PIXIS Princeton Instruments). When using the 2400 grooves/mm grating, the spectral resolution is improved up to 0.05 nm.

CL spectroscopy is performed on the same samples as for PL. They are placed on an tantalum sheet or on an electron microscope grid (for the spatially resolved spectra). Cooling of the sample is achieved at about 120 K. Samples are imaged using a 20 keV, 20 nA electron beam in a scanning electron microscope (JEOL 840). Using standard empirical models, the penetration depth is estimated to be about 2 μm, i.e., much larger than the sample thickness. A UV optimized and achromatic system (Horiba Jobin Yvon SAS) is used to analyze the CL emission in the 1.24–6.2 eV (200–1000 nm) range. The light is collected with a parabolic mirror and reflected using metallic coated optics into a monochromator (TRIAX550) equipped with two diffraction gratings (600 and 1800 grooves/mm) and a UV-enhanced silicon CCD camera. Under these conditions used here, the spectral resolution is 0.9 nm and 0.3 nm with 600 and 1800 grooves/mm gratings, respectively.

III. EXPERIMENTAL RESULTS

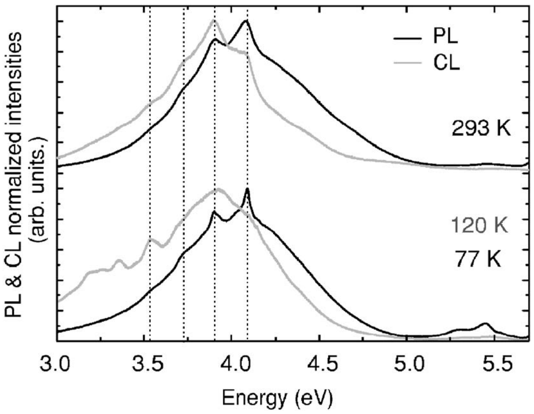

FIG. 1. Photoluminescence and cathodoluminescence spectra of h-BN at room and low temperatures. They are not corrected for system response. The photoluminescence spectra are excited at 5.82 eV.

CL and PL experiments performed at various temperatures exhibit strong luminescence bands at 4 and at 5.5 eV (Fig. 1). The two luminescence bands have been selectively probed by using the two available laser frequencies in PL (266 and 213 nm). CL and PL spectra have been recorded at room temperature and at 120 K for CL experiments and 77 K for PL ones. Both spectra display similar behaviors. At room temperature, a broad blue band located at 4 eV has a noticeable periodic substructure as well as a weak continuum near 5 eV. Finally, both CL and PL spectra exhibit a second well-defined band around 5.5 eV which appears distinctly at low temperature.

A. The 4 eV blue emission band

Whatever the temperature is, the band observed at 4 eV displays a periodic structure and identical spectral positions are measured in both PL and CL spectra, but the relative intensities between the two luminescence bands at 4 and at 5.5 eV differ. Such a variation in relative intensities was already observed in h-BN and is believed to depend on excitation conditions [current, voltage (CL), and laser frequency (PL)].[15] The two luminescence bands are characteristic of h-BN according to other observations by means of CL and PL spectroscopies. In those studies,[12,13] the 4 eV band was observed and, certainly erroneously, assigned to a band gap located at about 4 eV,[10,11] whereas Watanabe *et al.*[1] attributed it to the transitions due to impurity levels.

For the pure h-BN single crystal,[1] at room temperature, the ratio of the PL intensities between the two 5.5 eV bands and the 4 eV bands is equal to 100, whereas in our case this ratio is reversed. At room temperature, we find ratios equal to 0.06 and 0.03 in PL and CL, respectively, and at lower temperature, they become equal to 0.12 and 0.03. In comparison with other III-N materials,[16] we can assume that these relative intensities are consistent with an interpretation where the luminescence contributions to the 4 eV band are due to impurities or structural defects. Similar ratios have indeed already been observed in materials such as GaN.[17] Pure GaN crystal luminescence presents only one near-band-edge band, while addition of impurities, dopants (Si), Ga or N vacancies, or dislocations generates a broad yellow band[18]

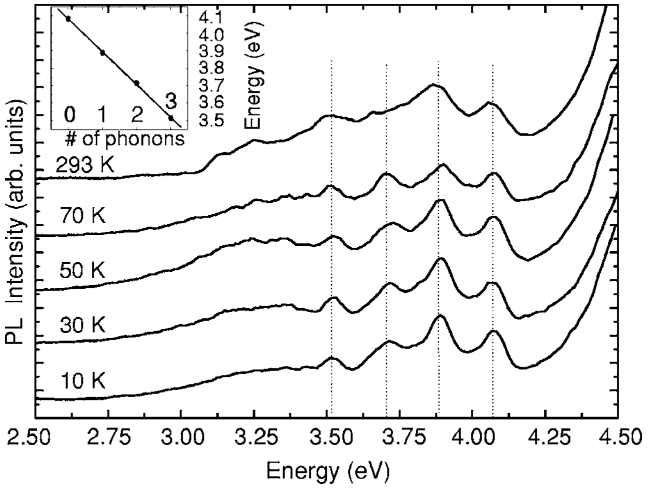

FIG. 2. PL spectra of h-BN excited at 4.66 eV from 293 K down to 10 K. Inset: number of the phonon replica as a function of the peak energy (resolution=0.02 eV).

(for a recent review see Ref. 19). The intensity ratio between the two bands varies from sample to sample and depends on the crystal quality and purity[17,20] and also on the excitation intensity, especially in the case of CL (see the discussion at the end of this section on saturation effects). Concerning h-BN, experimental[21] and theoretical studies[22–24] show that the most stable impurities and defects are C impurities and N vacancies or, to a lesser extent, N interstitials.

To probe the substructure of the 4 eV broad band in more detail, PL was performed using a laser wavelength set at 266 nm (4.66 eV) at temperatures ranging from room temperature to 10 K (Fig. 2). Four regularly spaced peaks can be seen in the band, which we assign to phonon replica. At low temperature, the linewidth of the phonon replicas sharpens, which allows us to determine spectral positions at 4.07, 3.89, 3.71, and 3.52 eV ± 10 meV and hence an average interval of 183 meV or 1480 cm^{-1}. We associate them to the zero, one, two, and three phonon lines, respectively. The spectral position of each peak seems to be independent of the temperature.

High-resolution PL was performed at 213 nm (5.82 eV) in order to determine more precisely the spectral interval between the phonon lines, i.e., the phonon frequency involved in these transitions (Fig. 3). This frequency can be estimated to be between 1390 and 1570 cm^{-1} with an average value of 1480 cm^{-1} similar to that determined previously. Each replica, however, displays complex substructures which may well indicate that several phonons are involved. Notice that, as expected, the zero-phonon line is narrower (about 23 meV) than the one-phonon line (about 36 meV). It is now placed at 4.10 eV; this is not significantly different from the position determined above which, furthermore, is slightly affected by the Rayleigh scattering induced by the proximity of the laser line (see Fig. 2). The linewidths are comparable to those reported very recently in the cubic zinc-blende structure of boron nitride (c-BN).[25]

In addition, a Raman spectrum has been recorded at the same temperature (77 K) and at the same laser frequency (213 nm). A Raman shift of 1365 cm^{-1}, which is typical of the B-N E_{2g} vibrational mode (LO mode), has been measured,[26,27] but no detectable Raman signal has been found between 1400 and 1600 cm^{-1}. This result differs from that by Wu *et al.*,[10] who find identical replica and Raman frequencies. Our data show unambiguously that the replica frequency is higher than the LO h-BN phonon frequency measured in Raman spectroscopy. On the other hand, calculations predict that, as a consequence of the coupling between the planes of h-BN, there is another high-frequency LO E_{1u} mode (1610 cm^{-1}) which is not Raman active, but which seems to have been observed from infrared reflectivity measurements.[26] This LO mode could be involved in the replica, but its frequency, which has to be confirmed, is fairly high, and it is more plausible to attribute them to a localized vibration coupled with the electronic deep levels. Similar effects have already been observed in diamond.[28]

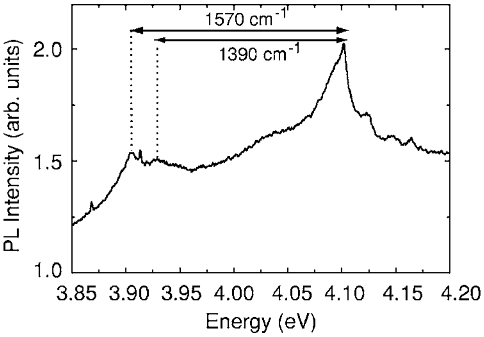

FIG. 3. High-resolution PL spectrum at 77 K showing the zero-phonon and the first-phonon lines of h-BN excited at 5.82 eV (resolution=0.0007 eV).

As a matter of fact, this value is close to the C-C E_{2g} stretching mode of a graphene sheet. Since the deep levels are presumably associated with C impurities, it can be suggested that the replica are due to local vibrational modes involving carbon atoms. Oxygen atoms or vacancies could also be involved. Let us also mention that recently Remes *et al.* have measured similar replica in photoconductivity spectra on h-BN single crystals.[29] Further studies are obviously necessary to elucidate the nature of this vibration mode and of its coupling with the deep electronic levels.

Finally, PL experiments were performed at various laser power densities (from 1.6 to 240 mJ/cm^2). Whatever the temperature is, the PL intensity of each peak increases linearly with the energy. No saturation was observed in this energy range. From similar observations, Wu *et al.*[10] conclude that such a behavior is typical of band-to-band optical transitions, which is unlikely as argued previously. This absence of saturation effect might simply be due to a high concentration of defects and to the still fairly low excitation density. Preliminary results on spatially resolved cathodoluminescence experiments at various excitation intensities actually show that the blue band saturates while the 5.5 eV emission band still increases (Fig. 4). Similar effects have been studied in detail in the case of GaN where strong nonlinear effects are observed. In the case of CL, in particular, strong excitations can be achieved by changing the electron beam current as well as the characteristics of the scanning electron microscope.[30–33] These observations strongly sup-

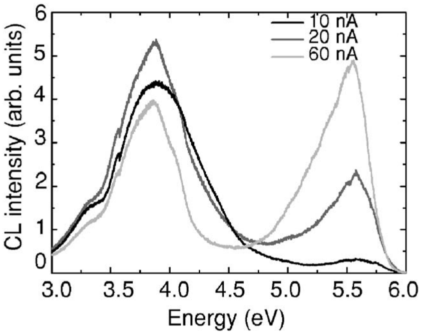

FIG. 4. Spatially resolved cathodoluminescence spectra at 298 K of h-BN crystallites at various applied currents.

port that the blue band emission is due to generic defects of the structure. This is also in complete agreement with recent studies concerning c-BN.[25]

B. 5.5 eV UV emission band

Figure 5 shows high-resolution CL and PL spectra in the near-band-gap region performed at low temperature. Four peaks located at 5.35, 5.48, 5.76, and 5.88 eV can be identified in the CL spectrum. The CL emission intensity vanishes at 5.96 eV, which is close to the "band-gap" energy (5.975 eV) reported by Watanabe *et al.*[1] Under these experimental conditions, the PL spectrum allows us to resolve two additional components at 5.56 and 5.64 eV. The absence of these components in CL is certainly due to the high excitation current densities used (about 2 A/cm^2).

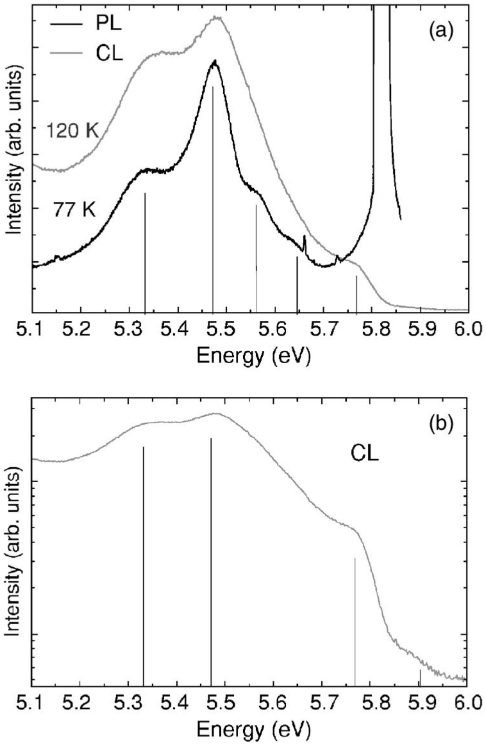

FIG. 5. (a) PL spectra of h-BN at 77 K excited at 5.82 eV and CL spectra of h-BN at 120 K. (b) CL spectrum in a logarithmic scale.

The PL laser excitation (213 nm), however, is not able to probe the highest radiative electronic states at 5.96 eV. The widths of our peaks are larger than those measured by Watanabe *et al.* (but similar to those reported by Taylor *et al.*[12]) and this certainly results from the quality of the sample. The agreement between CL experiments, PL experiments, and previously reported CL experiments unambiguously demonstrates the intrinsic character of the different spectral components of the 5.5 eV UV emission band. As explained before, recent calculations of the electronic structure assign the 5.5 eV UV emission band to free excitons with a binding energy of 0.72 eV (referred to the direct band gap).[5] The CL study of Watanabe *et al.* shows a predominant component at 5.765 eV (215 nm), whereas such a peak is not resolved in our experiments. Here again the differences can be partly due to our larger excitation current densities. The densities used by Watanabe *et al.* varied between 0.2 and 860 mA/cm^2.

In our PL spectra, the laser excitation line (5.82 eV) prevents a proper investigation of this particular spectral component. PL experiments with higher laser excitation frequencies are in progress as well as CL and PL experiments as a function of the excitation power, which should give more precise information on the nature of the different components of the 5.5 eV UV emission band.

IV. CONCLUSION

In conclusion, a combination of CL and PL spectroscopies has been used to determine the intrinsic h-BN luminescence properties. h-BN displays two separate emission bands, a deep-level broad band located around 4 eV, which is composed of a regular substructure and a near-band-gap peak around 5.5 eV. The deep-blue broad band (about 4 eV) reveals vibrational sequences attributed to phonon replica whose characteristic frequency is larger than the h-BN phonon frequencies measured by Raman spectroscopy. Since many theoretical and experimental arguments show that the optical band gap of h-BN should be in the range of 5.5–6 eV, we assume that this blue band is similar to the yellow band of GaN and should be associated with the presence of defects, presumably carbon or oxygen impurities, or vacancies, which can induce local vibration frequencies larger than those of the host.

PL spectra of the near-band-gap region reveal four components below 5.82 eV (laser excitation) intrinsic to h-BN. CL spectra display two additional bands at 5.76 and 5.88 eV which cannot be observed in PL because of the limited available spectral window. The position of these emission lines agree with those obtained by Watanabe *et al.* but are attributed here to (quasi-) Frenkel excitons. As mentioned in the Introduction, the main argument for that is based on recent theoretical analyses.[4,5] Although they do not agree in all details, these works completely agree to predict strong excitonic effects, which are expected anyway for such large band-gap compounds. They are so strong that their description in terms of usual Wannier-Mott excitons is certainly irrelevant here. More detailed analyses as well as investigations of BN nanotubes are in progress.

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