

Near band-gap photoluminescence properties of hexagonal boron nitride

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Graphite-like hexagonal hBN is most studied polymorph of boron nitride. The interest has been recently enforced by observation of far-UV lasing (215 nm) in single hBN crystal under electronic excitation [1]. However, despite of many experimental and theoretical efforts, its electronic and optical properties remain largely unknown. In present communication we report on detailed experimental study of low-temperature near band-gap luminescence of hBN excited with synchrotron radiation (SR). Low-intensity SR enables observation of excitonic and DAP transitions in conditions almost free of undesirable excitation saturation effects. Owing to spectral and time-resolved measurements we give evidences about the nature of the observed luminescence bands.

The studied samples were compacted from commercial hexagonal BN powders (Alfa 99.5%) in a square pallet (8x8x1 mm³) under a hydrostatic pressure of 0.6 GPa. The estimated grit size of the hBN powder ranged from 0.3 to 10 µm with an average particle size of 3.1 µm corresponding to the maximum in the mass distribution curve. Before measurements the samples were heated at 800 K under vacuum for 12 hours to avoid contamination by organic impurities and water. The measurements were performed at the SUPERLUMI station of HASYLAB at synchrotron DESY. Briefly, samples are cooled down to 8K and irradiated by monochromatized ($\Delta\lambda=0.3$ nm) SR under high vacuum ($\sim 10^{-9}$ mbar). The luminescence spectra and decay curves were measured using a visible 0.275-m triple grating ARC monochromator equipped with CCD detector or photomultiplier (HAMAMATSU R6358p). The recorded spectra were corrected for SR intensity, primary monochromator reflectivity and CCD sensitivity.

A series of high-resolution photoluminescence spectra of hBN in near band-gap region are presented in figure 1. Three relatively narrow bands at $E_{lum} = 5.47$ eV, 5.56 eV and 5.61 eV can be resolved. They appear with excitation above $E_{exc} = 5.7$ eV and their spectral positions don't depend on excitation energy. Conversely, a broader band detected at lower energy undergoes a strong energy shift with the excitation energy. This remarkable difference in spectral behaviour of 5.3 eV and 5.5-5.6 eV bands strongly suggests their different origins. This conclusion is supported by time resolved luminescent spectra (not shown). Three luminescence bands at 5.47 eV, 5.56 eV and 5.61 eV show a similar quasi-monoexponential (95%) decay with the characteristic time of 2.5 ns, whereas the shape of the 5.3-eV band decay is clearly multiexponential and becomes slower when the probed E_{lum} energy decreases.

We have assigned the three narrow bands around 5.5 eV to radiative transitions of bound excitons caused by disorder such as stacking faults or shearing of the lattice planes [2,3]. On the other hand, the multiexponential decay of the 5.3 eV band suggests a luminescence resulting from donor-acceptor pair transitions (DAP).



The most striking feature of the 5.3 eV band is its large blue shift (~ 120 meV) when the excitation energy increases. Two regimes can be however distinguished. (i) For excitation above 5.7 eV the band position is fixed at 5.3 eV. (ii) For excitation below 5.7 eV the band position E_{lum} varies linearly with excitation energy E_{exc} . In case of the selective DAP excitation, such dependence is expected with a slope $E_{lum} / E_{exc} = 1$. In contrast, a linear fit of the experimental data results in a slope $E_{lum} / E_{exc} = 0.66$, which indicates that the energy difference $E_{lum} - E_{exc}$ is not constant. This variable shift between E_{lum} and E_{exc} shows that a majority of the excited charge carriers do not annihilate on the initially excited DAPs and relax toward lower-energy

DAPs. The observed luminescence therefore involves DAP states different from that originally excited. This conclusion is supported by the constant spectral width (~ 180 meV) of the emission band, whatever is the excitation energy.

DAP transitions (1) usually undergo a blue shift with increase of the excitation intensity, as more charges are excited per unit crystallite volume. This is explained by the fact that donors acceptors are forced to be closer to each other, then the Coulomb interaction between them causes an increase of the transition energy $h\nu_{DAP}$. However, the classical DAP recombination model cannot accommodate the linear dependence between excitation photon energy E_{exc} and luminescence energy E_{lum} with a slope <1 , as well as the strong blue shift observed in present experiments. This suggests a recombination process involving Coulomb band fluctuations induced by random distribution of charged defects in the material. The amplitude Γ of such fluctuations increases with the concentration of charged defects and decreases with that of free carriers. This affects the energy of so-called quasi-DAP (q -DAP) transitions by twice the averaged fluctuation amplitude [4]

$$h\nu_{q-DAP} = h\nu_{DAP} - 2\Gamma \quad (2)$$

We used the q -DAP model to explain the shift of the 5.3-eV band. An observation of the Urbach tail in the excitation spectrum of this band supports a presence of the electrostatic potential fluctuations. As the excitation photon energy E_{exc} increases the absorption coefficient increases too. Increasing the excitation energy then produces similar effect as increasing the excitation intensity. In both cases, more photocarriers tend to neutralize more charged defects. This results in decrease of the fluctuation amplitude Γ and in subsequent increase of the transition energy (2). As a result, the energy difference $E_{lum} - E_{exc}$ is not constant in agreement with the experiment.

This work is supported by the by the IHP-Contract HPRI-CT-1999-00040 of the European Commission.

References

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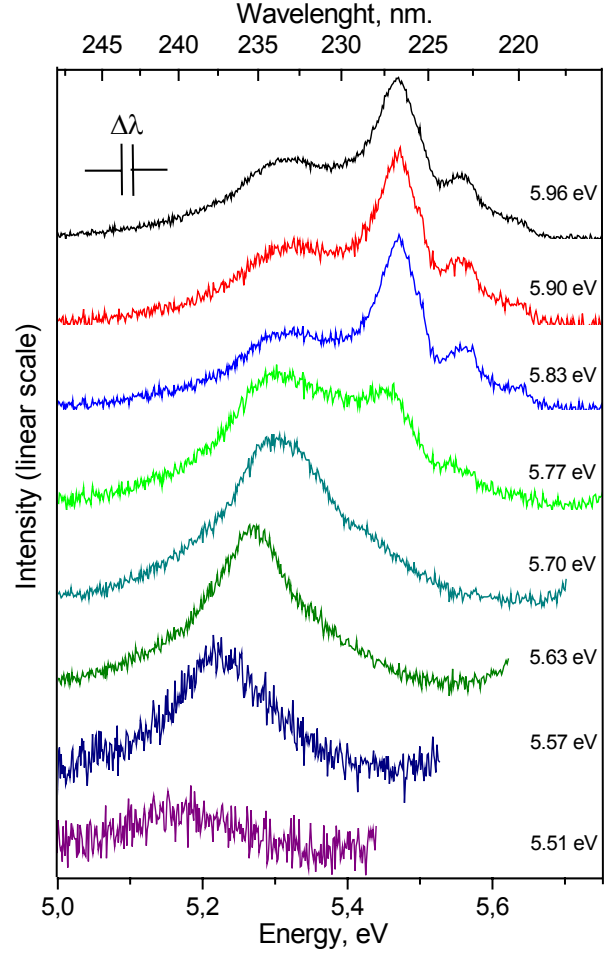


Figure 1: Near band-gap luminescence spectra of hBN for excitation energy E_{exc} .