Luminescence Dynamics of Defects in Boron Nitride of Different Stacking.

K. P. Korona[1], J. Iwański[1], K. Nogajewski[1], A. K. Dąbrowska[1], K. Watanabe[2], T. Taniguchi[2], J. Binder[1], A. Wysmołek[1]

[1] *Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland*

[2] *National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan*

Boron nitride (BN) is a wide band-gap material with honeycomb structure like graphene but instead of two carbon atoms there are B and N atoms. It breaks an inversion symmetry, so when next layer is rotated by 60º (A' form) one gets different pattern. The layers can be also shifted to B or C positions which leads to different stacking sequences (polytypes). The most popular are polytypes of AA' (called h-BN), AB (b-BN) and ABC (r-BN) stacking sequences. In the present work we show photoluminescence (PL), time-resolved PL and PL excitation (PLE) spectra of samples with different stacking order. The photoluminescence was excited by 3rd and 4th harmonics of Ti:Sapp laser (210 – 330 nm). Time-resolved photoluminescence was measured using a streak camera. The experimental part was performed mostly on BN grown on the MOVPE. We also measured some bulk samples of h-BN grown using Ba-BN solvent under HP-HT conditions and commercial samples obtained by chemical reaction. The stacking order of the samples was known from X-ray diffraction and electron microscopy.

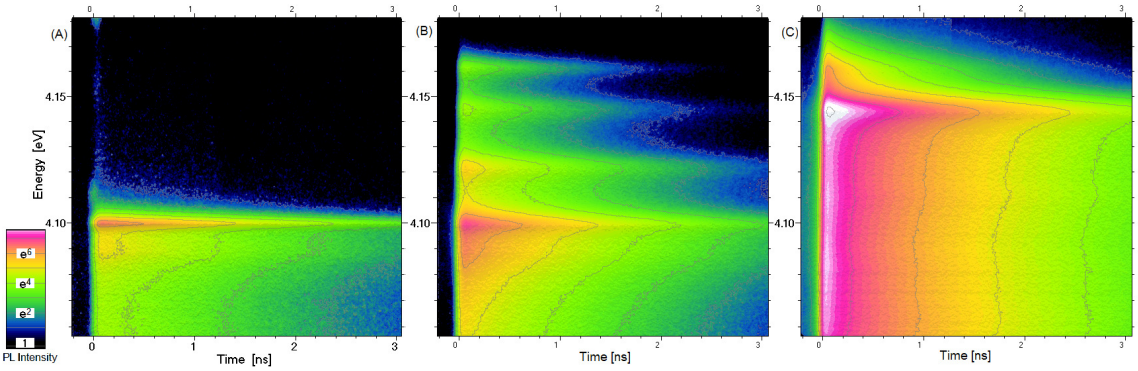

Figure: TRPL spectra of 3 different BN samples: A) pure AA', B) mixed AA' and AB, C) ABC stacking order (h-BN, h-BN plus b-BN and r-BN polytypes).

In the photoluminescence a donor-acceptor (or DX) emission at 5.3 - 5.4 eV was observed. Moreover, a band at about 300 nm was measured. The 300-nm band consisted of few sharp lines with nearly identical lifetimes. The detailed analysis reveals zero-phonon lines (ZPL) about 4.1 eV followed by a series of phonon replicas. Based on the previous publication [1] we postulate that the 300-nm lines can be assigned to C_BC_N defect and different energies of zero-phonon line are due to different stacking of the investigated samples. The ZPL were at slightly different positions in different materials, precisely at 4.096 eV (C302), 4.143 eV (C299) and 4.16 eV (C298) for h-BN, r-BN and b-BN polytypes. The E_{1u}(LO) phonon replicas were at at 3.90 eV and 3.94 eV for the C302 and C299 ZPLs. PLE results show that the Stokes shifts of the ZPL is minimal and that PL is very efficiently excited at an energy of E(ZPL)-0.2 meV (E_{1u}(LO) phonon). The lifetimes were of the order of 1 ns, precisely τ = 0.98 ns and 0.79 ns for the best AA' and ABC samples. The lifetimes were shorter in samples with mixed staking. For example, the longest lifetime of AB –related peak was found τ = 0.76 ns, but it was shortened to 0.14 ns in ABC with AB mixture. This and efficient excitation mentioned above suggest very fast excitation transfer between PL centers.

[1] T. Korona, M. Chojecki, Int. J. Quantum Chem. 119:e25925 (2019)