

Low temperature CL investigation of BN1 vibronic structure in c-BN

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Abstract

A full vibronic spectrum has been measured for the first time by LNT Cathodoluminescence in HPHT c-BN amber-coloured microcrystalline samples. The related BN1 centre at 3.293 eV seems not created by electron irradiation in this case and the accurately determined phonon energy (141 ± 3 meV) could be related to LO phonon at *X* point in Brillouin Zone (BZ) of c-BN, as determined by CL results obtained at indirect gap. Consequently, BN1 centre has not the full cubic symmetry of c-BN, as being due to N interstitials. The interpretation of the results is possibly two-fold: either we are observing a vibronic spectrum with ZPL at BN1 centre, together with other two centres called PF-1 and PF-2 at 3.573 and at 3.412 eV, respectively, or, since all the 6 or 7 observed peaks are exactly equally spaced, the whole vibronic spectrum is related to a ZPL line at 3.573 eV. This new interpretation seems to be in better agreement with the general theory of colour centres.

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1. Introduction

Cubic boron nitride (c-BN) is a wide band gap semiconductor still in an early stage of development with respect to diamond, but with the advantage of being the stable phase at room temperature and of being easily doped both p and n type, a fact that opens the way to several kinds of possible devices. More than 25 different centres have been discovered until now not only in HPHT (High Pressure High Temperature), but also in CVD deposited c-BN: many of them are created by irradiation and their importance is based both on the possibility of future production of ion implanted devices and also on the likely use of c-BN devices in a radiation hard environment.

The major difference with respect to diamond is related to the existence of off-stoichiometry and to the binary nature of c-BN, with the consequence of a larger variety of native defects, and to the polar nature of the B–N bond (25% ionic in character), which gives rise to polar longitudinal optical phonons (LO) strongly interacting with incident or emitted light. The investigations on these centres are carried out by PhotoLuminescence (PL), by CathodoLuminescence (CL) and by IonoLuminescence (IL or IBIL, Ion Beam Induced Luminescence) [1–5]. Also Raman

spectrum of c-BN has been extensively investigated [6–9]. Centres have been reported from 1.55 up to 4.05 eV, being generally the radiation-induced centres such as RC1, RC2, RC3, etc., much more intense than “natural” centres such as PF1 and PF2, for instance [1]. One of the more recently reported centre, indicated as BN1, was found in electron irradiated samples (230–300 keV, about 10^{20} e/cm²), with a ZPL (Zero Phonon Line) placed at 376.4 nm (3.293 eV) and with some phonon (LO, TO) replicas at the anti-Stokes side [1]. Because of its similarity with the 3.188 eV centre in electron irradiated diamond, attributed to interstitial nitrogen, and also because calculations [8,9] indicate a lower formation energy for N_i with respect to B_i, it was concluded that this centre was created only during electron irradiation. Raman spectra quote very consistently a LO phonon line at 1305 cm⁻¹ (161.5 meV) and a TO line at 1054.7 cm⁻¹ (130.5 meV) [7] and these values are in close agreement with phonon replicas reported previously at 7 K under 325 nm excitation, from which a LO energy between 159.7 and 163 meV can be evaluated from the quoted PL spectrum. The authors report that below 200 keV only very weak BN1 luminescence was observed under UV illumination, which completely disappeared after irradiation at 150 keV. CL seems to be a more powerful method with respect to excitation mode, which does not follow specific selection rules and can fill up any radiative recombination centre. In fact [10] by CL some phonon-assisted free-exciton luminescence lines were

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