

Vibronic spectrum of *c*-BN measured with cathodoluminescence

C. Manfredotti,* R. Cossio, A. Lo Giudice, E. Vittone, and F. Fizzotti

*Experimental Physics Department and Center of Excellence NIS, University of Torino, Torino, Italy
and National Consortium for Matter Science, CNISM, Italy*

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An extended vibronic spectrum (up to six phonon replicas) has been measured by low temperature cathodoluminescence in pure *c*-BN microcrystalline samples obtained by high temperature high pressure method. The zero phonon line, found at 3.573 eV, should be connected to a center identified previously as PF1, which is intrinsic in *c*-BN. As a consequence, the vibronic spectrum is not associated with the BN1 center at 3.293 eV, which is created by irradiation, as reported in literature. The spectrum is in very good agreement with the Franck-Condon model, formerly developed for color centers in alkali halides and from which in this case a value of 5.26 for the Huang-Rhys factor can be obtained. From the spectrum it has been possible to determine very precisely the value of phonon energy (141 ± 3 meV), which is in good agreement both with the results of *ab initio* calculations of LO phonon energy at the *X* point of the Brillouin zone of *c*-BN and with the value measured by second-order Raman spectroscopy. The connection of this center with the indirect gap and the large energy threshold for excitation could explain why this center with its vibronic band was hardly seen before by photoluminescence. Since the measured displacement of the equilibrium normal coordinate of the excited level was found to be 0.17 nm, this level could be attributed, according to calculations from first principles, to a boron antisite and not to a Frenkel pair (a nitrogen vacancy coupled to a boron interstitial) as previously indicated.

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I. INTRODUCTION

Cubic boron nitride (*c*-BN), in a way similar to diamond, has a diamond-like zinc blende structure, but it can exist in forms such as graphite-like hexagonal (*h*-BN), lonsdaleite-like wurzite (*w*-BN), disordered turbostratic (*t*-BN), and rhomboedral (*r*-BN). Among all these isomeric compounds, and also among all the other covalently bonded materials known so far, *c*-BN has the largest energy gap and, consequently, it is expected to be a technologically important material for deep blue and UV applications. Moreover, with respect to diamond, *c*-BN can be *p*- or *n*-doped and it does not react with Fe at any temperature. A still debated question concerns its stability at ambient atmospheric conditions. One consideration could be that, at least from a theoretical point of view, *c*-BN is stable at room temperature, while, in the case of diamond, the stable phase at room temperature is represented by graphite. In fact, in contrast to previous suggestions given by Corrigan-Bundy equilibrium phase *p*-*T* diagram,¹ it has been shown more recently that the equilibrium line between *c*-BN and the hexagonal phase *h*-BN intersects the temperature axis at 1570 K,² with the conclusion that up to 1600 K the thermodynamically stable boron nitride modification is the cubic and not the graphite-like one as it was previously thought. From an experimental point of view, it is known from HPHT (high pressure high temperature) synthesis that at 1300 K *h*-BN is the stable phase,³ while below this temperature *c*-BN could be more stable than *h*-BN.

The question arises now whether BN films undergo phase transitions or structural changes upon annealing to temperatures as high as 1400 K. One important aspect is represented by the high compressive stresses, which are reported in the range from 3 to 15 GPa and which have hampered the commercialization of this material.⁴ In fact, these stresses cause

adhesion problems in the case of growth or deposition by CVD (chemical vapor deposition), since in this case film thickness is limited to 200 nm. Better results are however obtained by PECVD (plasma enhanced CVD) in the ECR (electron cyclotron resonance) version, by which *c*-BN samples of thickness of several micrometers with much lower stress levels have been deposited.⁵ More than 25 different centers have been discovered until now not only in HPHT 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 differences with respect to diamond are 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. From another point of view, the polar nature of the B-N bond with respect to diamond (bonds are 25% ionic) gives rise to polar longitudinal-optical phonons (LO) strongly interacting with incident or emitted light. Previous investigations on native defects were carried out by photoluminescence (PL), by cathodo-luminescence (CL), and by ionoluminescence (IL or IBIL, ion beam induced luminescence).⁶⁻¹⁰ Also, Raman spectrum of *c*-BN has been extensively investigated.^{11,12} Luminescence centers have been reported in the energy region from 1.55 to 4.05 eV; radiation-induced centers, such as RC1, RC2, RC3, etc., are much more intense than "natural" centers such as, for instance, PF1 and PF2.³ One of the more recently reported centers, indicated as BN1, was found in electron irradiated samples (up to a dose of 10^{20} cm⁻² at about 3×10^5 eV). This center seems to display a ZPL (zero phonon line) at 376.4 nm (3.293 eV) together with some phonon (LO, TO) replicas.³ Because of its similarity with the 3.188 eV center