Available online at www.sciencedirect.com

ScienceDirect

Journal of Luminescence 127 (2007) 595–600

JOURNAL OF LUMINESCENCE

www.elsevier.com/locate/jlumin

Photoluminescence of hexagonal boron nitride: Effect of surface oxidation under UV-laser irradiation

Luc Museur[a,*], Demetrios Anglos[b], Jean-Pierre Petitet[c], Jean-Pierre Michel[c], Andrei V. Kanaev[c]

[a]Laboratoire de Physique des Lasers – LPL, CNRS, Institut Galilée, Université Paris 13, 93430 Villetaneuse, France
[b]Institute of Electronic Structure and Laser (IESL), FORTH 711 10 Heraklion Crete, Greece
[c]Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions – LIMHP, CNRS, Institut Galilée, Université Paris 13, 93430 Villetaneuse, France

Received 19 September 2006; received in revised form 16 January 2007; accepted 22 January 2007
Available online 4 April 2007

Abstract

We report on the UV laser-induced fluorescence of hexagonal boron nitride (h-BN) following nanosecond laser irradiation under vacuum and in different environments of nitrogen gas and ambient air. The observed fluorescence bands are tentatively ascribed to impurity and mono (V_N) or multiple (m-V_N with m = 2 or 3) nitrogen vacancies. A structured fluorescence band between 300 and 350 nm is assigned to impurity-band transition and its complex lineshape is attributed to phonon replicas. An additional band at 340 nm, assigned to V_N vacancies on surface, is observed under vacuum and quenched by adsorbed molecular oxygen. UV-irradiation of h-BN under vacuum results in a broad asymmetric fluorescence at ~400 nm assigned to m-V_N vacancies; further irradiation breaks more B–N bonds enriching the surface with elemental boron. However, no boron deposit appears under irradiation of samples in ambient atmosphere. This effect is explained by oxygen healing of radiation-induced surface defects. Formation of the oxide layer prevents B–N dissociation and preserves the bulk sample stoichiometry.

PACS: 78.55.Cr; 78.55.−m; 68.43.−h

Keywords: Hexagonal boron nitride; Photoluminescence; Surface oxidation; UV-laser irradiation

1. Introduction

During the past years, electronic and crystalline structures of boron nitrides (BN) have been studied in detail, both theoretically and experimentally [1,2]. This is mainly due to important properties of BN such as high electrical resistance and thermal conductivity, extreme mechanical hardness, elevated melting point, large band gap energy that make this material interesting for many large-scale applications in electronics, optoelectronics, protective coating, etc.

Graphite-like hexagonal BN (h-BN) is the most commonly used polymorph of BN existing also as cubic (diamond-like), rhombohedral, and wurtzitic. The electronic structure of h-BN has been studied by luminescence [3–8], optical reflectance and absorption [9–12], X-ray emission [13–15], inelastic X-ray scattering [16,17], X-ray absorption [15,18,19], electron energy loss [20–22] spectroscopy. Despite extensive studies, up to now there is disagreement on its basic electronic properties. For example, both direct and indirect band gap natures and widely dispersed band gap energy values ranging from 3.6 to 7.1 eV have been reported in the literature [8]. The h-BN band structure theoretical calculations in the LDA approximation result in the lowest indirect gap around 4 eV [23–27], whereas recent GW calculations increase this value to 5.95 eV [27]. The effects of stacking on the electronic properties of h-BN have been studied [26] predicting the indirect band gap close to 4.0 eV for the most common form of h-BN.

---

*Corresponding author. Tel.: +33 1 49 40 37 24.
E-mail address: museur@galilee.univ-paris13.fr (L. Museur).

0022-2313/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2007.01.024

The interest in luminescence properties of h-BN has been recently renewed with observation of laser effect at 215 nm in monocrystalline sample under e-beam excitation [4]. Although the photoluminescence (PL) of many III–V group semiconductors such InP, GaAs, GaN, etc. has been extensively studied in the past, only few data exist in the literature about the BN PL. With excitation at $\lambda = 262$ nm Larach et al. [6] have observed a fine-structure luminescence in the range of 300–500 nm and considered it to be inherent to the BN molecular layer. Katzir et al. [28] have observed a blue PL continuum in the range of 390–500 nm ($\lambda_{exc} = 320$ nm) attributed to deep levels of carbon impurities. Afterwards, the effects of carbon doping on the blue luminescence has been studied by several groups [29–31]. Yao et al. [32,33] have investigated the visible PL dependence on a degree of three-dimensional sample ordering.

So far, the luminescent mechanism in h-BN is not clear and needs further investigations. A large diversity in shapes and positions of PL spectra published in the literature are usually interpreted on the basis of impurities present and sample preparation conditions. Some important parameters as environment, excitation intensity, and light-induced changes in samples have not been yet considered. In the present article we report on room temperature PL of h-BN following 248-nm laser irradiation below ablation threshold. We show influence of irradiation dose, fluence, and environmental atmosphere on PL spectra, which allows distinguishing between surface and bulk fluorescent centers. We underline the importance of the BN surface oxidation induced by UV irradiation in the presence of oxygen gas.

These results are of interest in the frame of the current research on BN nanotubes (NT) which are more oxidation resistant and are expected to have better electronic properties than carbon NT [34]. Recently, the attempts [35,36] to use PL measurements to recognize in situ BN NT mixed with microcrystalline h-BN have been limited by the lack of precise knowledge about h-BN luminescence. Moreover, the use of BN NT as UV light source could be complicated by the possibility of surface oxidation.

2. Experiment

Experiments were carried out at the IESL—FORTH using a nanosecond ($\tau_L = 15$ ns) KrF excimer laser ($\lambda = 248$ nm). The samples were placed in a homemade high pressure cell, with sapphire windows, which allows varying the pressure in the range from 10^{-2} mbar to 1 kbar [37]. The laser beam was focused on the sample surface at room temperature. The energy on the sample was changed by using two reflective attenuators and was carefully measured using an energy meter and taking into account the beam geometry. Typical laser fluence in fluorescence experiments was between 1 and 100 mJ/cm^2. The laser-induced fluorescence was collected by a quartz lens and focused on a multimode quartz optical fiber. A compact spectrograph equipped with a concave holographic grating, combined with an ICCD detector (DH520-18F, Andor Technology), was used to record the time-integrated emission spectrum from 200 to 800 nm with a resolution of about 2 nm.

In the experiments the UV laser has been used in two different modes of fluence. In the first mode, high fluence pulses (100 mJ/cm^2) and long irradiation periods are used to possibly induce transformations on the sample. In this way dose irradiation of several 100 J/cm^2 has been achieved. In the second mode, low fluence pulses (typically 2–3 mJ/cm^2) are used to probe the sample. Due to the accumulation of 500 luminescent pulses on the CCD detector, this corresponds to an irradiation dose of 1 J/cm^2. Except one, all the luminescent spectra presented in this article have been obtained with low fluence probe pulses.

The samples were square pallets ($8 \times 8 \times 1$ mm^3) compacted from h-BN powder (Alfa, 99.5%) under a pressure of 0.6 GPa. To avoid organic impurities and traces of water, the pallets were heated at 800 K under vacuum for a period of 12 h. The grit size of the h-BN powder used for the experiment has been estimated by granulometry and transmission electron microscopy (JEM 100C JEOL). It 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.

3. Results and discussion

The h-BN is a highly fluorescent material under optical excitation above 4 eV [8,38]. Its fluorescence spectra show different bands: (i) an asymmetric-shape continuum expanding into the visible with a maximum at 370 nm (UV1), (ii) a structured band with four maxima between 300 and 350 nm (UV2), and (iii) a broad visible continuum below ~400 nm (V1). The bands UV1 and UV2 have been earlier assigned correspondingly to the surface and bulk state emission. Their origins, however, are still debated. In our early studies [38] we have analyzed the effect of nanosecond laser irradiation (248 nm) on polycrystalline h-BN under vacuum. In short, it is resumed in surface enrichment by elemental boron due to B–N bond breaking [39]:

$$BN(s) + h\nu(5.0\,eV) \rightarrow B(s) + 1/2N_2(g), \qquad (1)$$

where (s) and (g) represent, respectively, solid- and gas-phase species. This photochemical process requires an activation energy of 2.57 eV that is smaller than that of the UV laser photons. The surface modification has been spectroscopically observed by a decrease of the intensity of characteristic UV emission bands [38].

Below we will discuss the nature of h-BN fluorescence bands appearing following nanosecond laser surface irradiation in different environments. The observed spectral features will be tentatively ascribed to mono and