

INFLUENCE OF AIR, OXYGEN, NITROGEN AND ARGON
ON 400 nm LUMINESCENCE IN HEXAGONAL BORON NITRIDE

V. Korsaks, B. Berzina, L. Trinklere

Institute of Solid State Physics, University of Latvia,
8 Kengaraga Str., LV-1063, Riga, LATVIA
e-mail: valdis.korsaks@gmail.com

The investigation is devoted to the influence of different surrounding gases on the defect-related luminescence in hexagonal boron nitride (hBN). The photoluminescence spectra of hBN powder were measured for an hBN sample placed in different surroundings formed by ambient air, vacuum, as well as oxygen, nitrogen and argon gases. It was found that the 400 nm luminescence caused by native defects in hBN is sensitive to the oxygen gas and ambient air. Presence of oxygen gas around hBN considerably reduces the intensity of this luminescence. The results evidence that hBN powder can successfully be applied as the material for oxygen sensors.

Key words: *photoluminescence, hexagonal boron nitride, oxygen sensor.*

1. INTRODUCTION

Hexagonal boron nitride (hBN) is a promising wide-band gap material for possible application as the light emitter within a far ultraviolet (FUV) spectral region [1]. This application is based on excitonic processes, therefore exciton luminescence is well studied in hBN materials with different modifications – such as single crystals, macrosized polycrystalline powders and nanotubes ([2] and Refs. therein).

The defect-related luminescence in hBN has not been so thoroughly examined. Wu *et al.* [3] report the luminescence of native defects in hBN to be within the wavelength region above 250 nm. One intensive band with a fine structure was observed at 320 nm and some others – in the 380-400 nm range. The 320 nm luminescence is sufficiently well investigated [4–6]. Recently, we studied luminescence of native defects in macrosized polycrystalline hBN powder and multiwall nanotubes (BNNTs) [7–9]. The native defects can be formed from impurities such as O and C atoms (which are characteristic for the boron nitride), and from various imperfections of the crystalline host lattice such as boron and nitrogen vacancies (v_B , v_N), as well as interstitials and Stone-Walls' defects where the number of atoms in the elemental hexagonal ring is changed. More intensive luminescence bands are observed at 320 nm and 400 nm, and their properties have also been studied [4–6].

The aim of our investigation was to reveal the influence of different surrounding gases on the native defect luminescence in hBN when the samples are placed in the ambient air, vacuum as well as oxygen, nitrogen and argon gases.

2. EXPERIMENTAL

We used hBN powder consisting of macrosized polycrystalline grains (*Aldrich Corp.*) The grain size of the material was estimated to be within 1 μm – 10 μm range, and the material purity was up to 99.5 atom%.

The sample for investigation was prepared inserting hBN powder into a special holder using light pressing. Before the measurements the sample was heated up to 420 °C in air to remove humidity, then cooled down to the room temperature (RT) and put into a special camera (the element of a CCS-100/204 cryostat (*Janis Research Co.*)) allowing realization of various environmental conditions. The gases used for filling the camera were: oxygen, nitrogen and argon, with purity of 99.5% and humidity of 200 ppm.

The setup for luminescence measurements consists of a deuterium lamp (400W) for luminescence excitation and two monochromators. One of them is used for filtering the exciting light and the other one (*Andor SR 303i*) together with a CCD camera – for recording the luminescence spectra visualized on the screen of display.

All measurements were taken at RT and normal atmosphere pressure of gases filling the cryostat camera with the sample.

3. RESULTS AND DISCUSSION

The photoluminescence (PL) spectra of hBN measured at RT and 266 nm excitation corresponding to different gases are shown in Fig. 1. The spectra are complex, consisting of two main bands at 400 nm and 320 nm resulting from the native defects. The first PL spectrum after the heating process (with the lowest intensity) was measured when the sample was in ambient air. In the figure it is seen that the 320 nm luminescence is predominant, and its intensity exceeds that of 400 nm. Afterwards, the air was pumped out from the camera and a vacuum level of $p = 3 \cdot 10^{-5}$ mbar was reached (solid curve with open circles). In Fig. 1 it is also seen that the intensity of 400 nm luminescence is growing for almost an order of magnitude, whereas that of 320 nm luminescence changes but slightly. The next step was filling the camera with oxygen gas, which resulted in a 38% reduced 400 nm luminescence, at the same time leaving the 320 nm luminescence unchanged. Then the oxygen gas was pumped out of the camera and the previous vacuum level was restored. The PL spectrum coincides with that measured previously under the same vacuum conditions. Filling the camera with nitrogen or argon gases does not affect the luminescence spectra, while in the case of its filling with ambient air (O ~ 21% and N ~ 79%) the 400 nm luminescence decreased by 17% (a bold solid curve in Fig. 1); after the air was pumped out it did not reach the previous level in vacuum as it was in the case of pure oxygen. This could be explained with the dispersion of experimental measurement data.

The above results clearly testify the influence of oxygen gas on the luminescence of native defects in hBN. Presence of oxygen gas in hBN reduces the intensity of 400 nm luminescence, at the same time not affecting the 320 nm luminescence. This means that bleaching of the 400 nm luminescence could be related to oxygen, because in the presence of nitrogen and argon gases no changes in the 400 nm PL were observed.

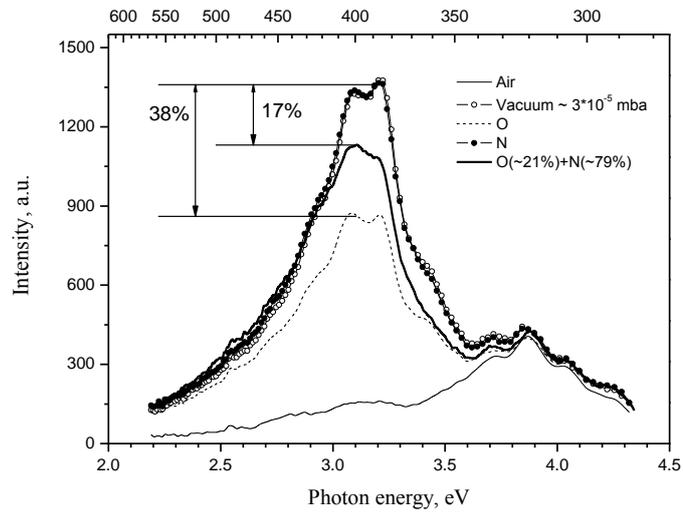


Fig. 1. Photoluminescence spectra of hBN powder (RT, 266 nm excitation) inserted in different environments: ambient air, vacuum, oxygen and nitrogen gases.

The spectral characteristics of 400 nm luminescence (see in our previous works [8, 9]) throw light on its nature. The spectrum of this photoluminescence and its excitation spectrum for hBN at RT are shown in Fig. 2. This defect-related luminescence forms a wide band with a phonon-induced substructure, which is characterized with two excitation bands resulting from two absorption bands of defects. Nevertheless, the defects forming the luminescence center remain unknown [10, 11]. The present investigation allows for the suggestion that these defects are situated either on the surface of the material or close to this surface being sensitive to oxygen from the gas surrounding the material. Regarding the 320 nm luminescence we can conclude that the corresponding luminescence centers are situated within the bulk of hBN and are not affected by environment conditions.

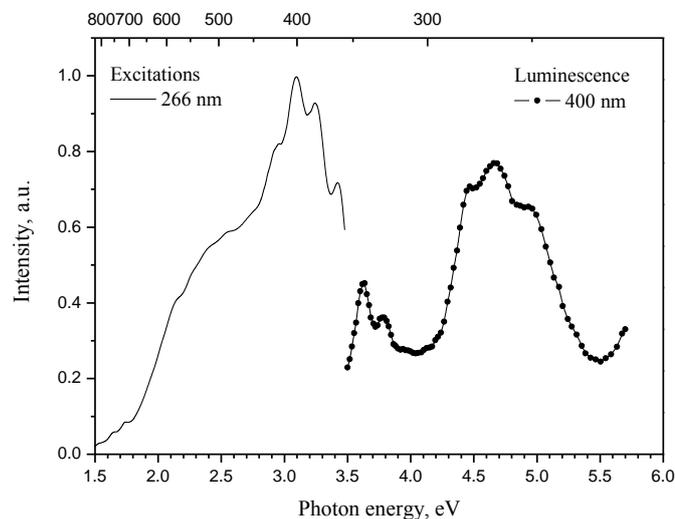


Fig. 2. Photoluminescence (solid curve) and its excitation spectrum (solid curve with black circles) of hBN at RT. The PL spectrum was measured at 266 nm excitation, and the luminescence excitation spectrum was obtained recoding 400 nm emission.

The sensitivity of 400 nm luminescence in hBN to the presence of oxygen in ambient surrounding evidences that this material is potentially applicable as the oxygen sensor. The necessary investigations are going on.

4. CONCLUSIONS

From the results of measurements it follows that the 400 nm luminescence originates from the native defects located on the material surface in hBN powder and is sensitive to pure oxygen gas and ambient air. The presence of oxygen gas on the hBN material considerably reduces the intensity of 400 nm luminescence. The phenomena observed present evidence for potential hBN application as oxygen sensor material.

ACKNOWLEDGMENTS

The present research was supported from the National Research Program "IMIS", European Social Funds (ESF) and from the European project ERAF Nr 2010/0253/2DP/2.1.1.1.0/10/APIA/VIAA/079 to which we are deeply grateful.

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HEKSAGONĀLĀ BORA NITRĪDA 400 nm LUMINISCENCES IZMAIŅA GAISĀ, SKĀBEKĻA, SLĀPEKĻA UN ARGONA GĀZĒS

V. Korsaks, B. Bērziņa, L. Trinklere

Kopsavilkums

Darbā pētīta dažādu gāzu ietekme uz hBN luminiscenci. Analizēti hBN fotoluminiscences spektri, paraugam atrodoties dažādās gāzēs: gaisā, skābeklī, slāpekļī, argonā, kā arī vakuumā. Ir atrasts, ka 400 nm luminiscenci, kura ir saistīta ar dabīgiem defektiem hBN, ietekmē gāzveida skābekļa sadarbība ar šo materiālu. Skābekļa klātbūtne ap paraugu ievērojami samazina 400 nm luminiscences intensitāti. Novērotā parādība ļauj prognozēt hBN materiāla pielietojumu skābekļa sensoru izveidei.

27.03.2012.