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Cathodoluminescence of carbon-related defects in hexagonal boron nitride

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Abstract. Hexagonal boron nitride is a wide band gap semiconductor exhibiting various luminescence bands in visible and near ultraviolet range, which can be used as single photon source. The luminescence band with zero phonon line at 4.1 eV is commonly ascribed to the carbon impurity introduced during crystal growth. In this paper we provide experimental evidence that carbon-related luminescent centers can be introduced in hBN by local electron irradiation in the chamber of scanning electron microscope at room temperature that can be used as a technique for the nanofabrication of single photon source devices with desired pattern.

1. Introduction

Hexagonal boron nitride (hBN) has been extensively investigated during last years and remains in demand because of its peculiar luminescent properties. Although the luminescence of hBN, particularly its cathodoluminescence (CL), started to be investigated beginning from 1950s [1], the most of accurate and important results were obtained only during last decade, so that the first report on band edge luminescence has been published only in 2004 [2], when high-quality single crystals been synthesized for the first time. Besides the band edge, several other luminescence peaks have been experimentally found in visible and near ultraviolet range. Theoretical calculation attributed them to various native defects and/or impurities introduced during the crystal growth [3].

Some of such light emitting centers were found to exhibit the properties of single photon sources, that are of a great interest for various applications in optoelectronics and that, in turn, gave a new rise to the investigation of luminescence of hBN few years ago [4]. The well-known single photon luminescence bands in hBN are two series of luminescence lines with zero phonon lines at 2.0 eV and 4.1 eV [5]. For 2 eV band diverse defects were considered as possible candidates such as dangling bonds, vacancies and their complexes [5,6]. As for 4.1 eV band, it was shown that its intensity correlated with the carbon impurity concentration in hBN [7] and, accordingly, various carbon-related defects of the luminescence center were proposed: substitutional carbon at nitrogen site (C_N) [4], substitutional carbon at boron site (C_B) [8], carbon dimer ($C_B C_N$) [8,9] and carbon-oxygen complex ($C_N O_N$) [10].



The listed ambiguity stimulates additional experimental investigations of the interaction between carbon and hBN. Of a particular interest is the search of a controllable local insertion of carbon impurity into hBN for the fabrication of single photon emitter devices of desirable design.

In this paper we demonstrate for the first time that local electron beam induced deposition of carbon-rich film onto the surface of hBN at room temperature resulted in the appearance of a bright 4.1 eV luminescence that can serve as a new nanofabrication technique of single photon sources.

2. Materials and methods

2.1. hBN samples

High purity single crystals of hexagonal boron nitride were grown in barrium boron nitride solvent as described in more details elsewhere [11]. The investigated samples were thin nanoflakes prepared by exfoliation of the crystals and deposited onto silicon nitride film on silicon. The thickness of diverse used flake as measured by atomic force microscopy varied from 14 to 170 nm.

Carbon-rich films were formed on the surface of hBN flakes performing rectangular scans with scanning electron microscope (SEM) electron beam at a current of 3 nA for 10 minutes as the result of the decomposition of residual hydrocarbons present in SEM chamber.

Two subsequent post-deposition treatment procedures were performed: 1) oxygen plasma (Ar/O₂: 95/10) at room temperature for 3 minutes using Fischione NanoClean plasma cleaner was performed in order to clarify whether the luminescent band stems from surface or the bulk, 2) annealing at 1000°C for 30 minutes in vacuum furnace was performed in order to test the mobility of introduced luminescence centers.

2.2. Cathodoluminescence investigation

Cathodoluminescence (CL) of the samples was investigated at room temperature using SEM Zeiss Supra 40VP equipped with Gatan MonoCL 3 detection system in a wavelength range from 250 to 700 nm with a spectral resolution of 1 nm. All CL spectra and intensity maps were recorded at an accelerating voltage of 5 kV and in continuous scanning mode at each stage of the experiments: for clean sample as is, after carbon-rich film deposition, after the oxygen plasma treatment and after the high temperature annealing.

3. Experimental results

3.1. CL of pristine hBN and effect of carbon-rich film deposition

CL spectrum of pristine hBN depicted in figure 1a) consists of dominated intense peak at 2.9 eV and the peak of lower intensity at 1.9 eV. No detectable CL signal at 4 eV was observed.

As a result of a prolonged electron beam scan dark contrast appeared within the scanned region on secondary electron images that is well-known to be caused by the decomposition of hydrocarbons presented in every conventional vacuum system. CL spectrum of the sample coated with carbon-rich film is depicted in figure 1b). Besides the peaks at 2.9 eV and 1.9 eV observed in pristine sample, a new CL band with unresolved fine structure and the main maximum peak position at about 3.9 eV appeared. One can also note that the shape of 2.9 eV line did not change noticeably while the spectral structure of 2 eV band remarkably changed that is believed due to second order diffraction grating reflection of the new carbon-related band.

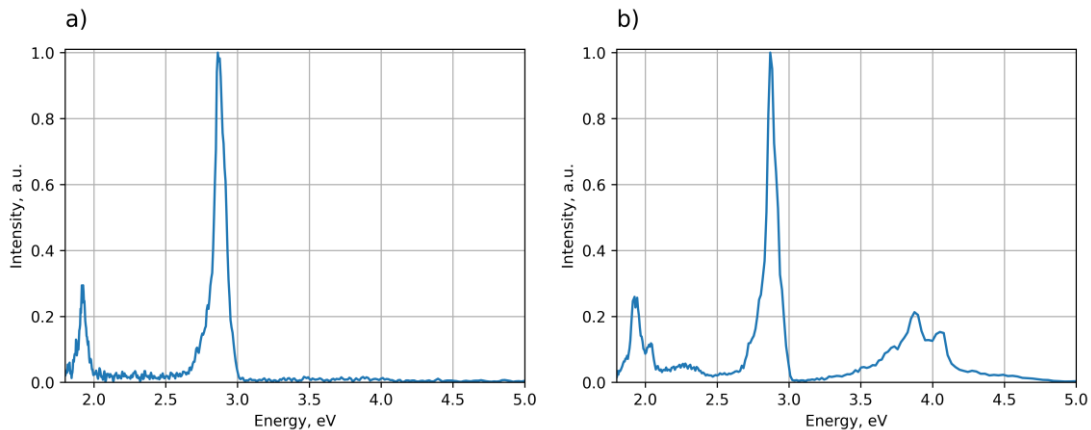


Figure 1. a) CL spectrum of pristine hBN sample, b) CL spectrum of hBN sample after local coating with carbon-rich film.

This new band can be deconvoluted into five narrow Gaussian peaks at 3.36 ± 0.03 eV, 3.53 ± 0.02 eV, 3.71 ± 0.02 eV, 3.88 ± 0.01 eV, 4.05 ± 0.01 eV and one broad band at 4.2 ± 0.5 eV as it demonstrated in figure 2. An energy separation between narrowest peaks was approximately 0.17 eV, which is in a good agreement with previously reported energy of LO phonons of 175 meV [10]. Thus, the series of the peaks was attributed to a zero phonon line (ZPL) at 4.05 eV accompanied with phonon replicas.

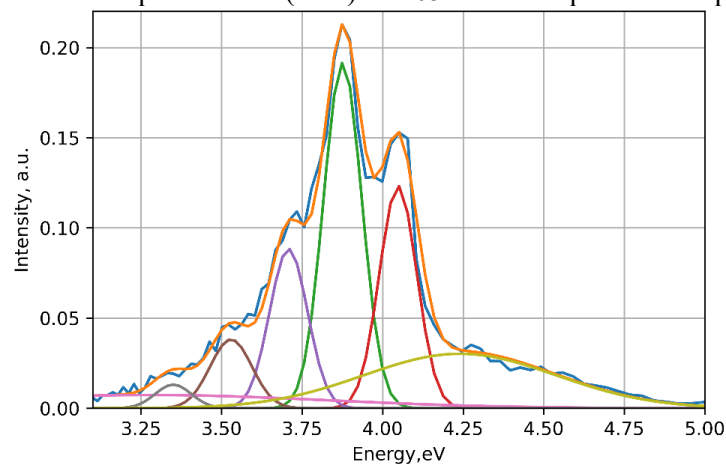


Figure 2. Deconvolution of 4.1 eV CL band.

3.2. Effect of oxygen plasma treatment on CL of carbon coated hBN

As expected, after the treatment the surface of the samples became clean without any traces of the dark stains visible in SEM images. Figure 3a compares CL spectra of the sample with deposited carbon-rich film before and after the treatment in oxygen plasma. As one can see from the figure 3a the integral CL intensity of the band reduced as the result of the treatment at the expense of high-energy part of the band.

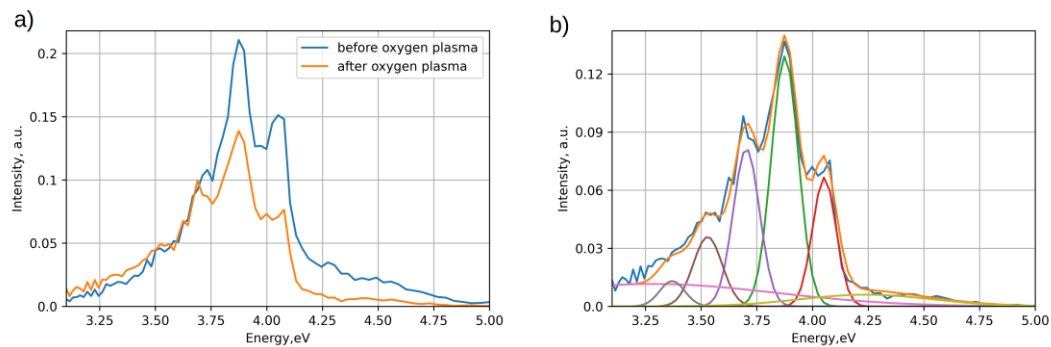


Figure 3. a) CL spectra of carbon coated samples before and after oxygen plasma treatment; b) deconvolution of 4.1 eV CL band for oxygen plasma treated sample.

Detailed analysis of the deconvolved components (figure 3b) revealed that the intensity of high energy broad band at 4.2 eV noticeably decreased, whereas the intensity and the position of all other peaks remained almost unchanged.

3.3. Effect of high temperature annealing

The sample treated in oxygen plasma was subsequently subjected to the annealing at 1000 °C in vacuum furnace. That resulted in complete disappearance of the high-energy broad band peaked at 4.2 eV, while the intensity of the main series of narrow peaks slightly increased without noticeable changes of their spatial distribution over the sample surface. The latter is demonstrated in figure 4 that shows monochromatic CL profile at 320 nm (4.1 eV) across the region where carbon was deposited. The edges of the profile are rather sharp indicating the absence of noticeable lateral migration of the luminescent centers from the region initially covered with carbon-rich film. One should also note rather high background CL signal outside of the central part of the profile that, most probably, was caused by the fact that the entire area of the sample during multiple SEM images acquisitions was repeatedly scanned with the electron beam stimulating the formation carbon related defects

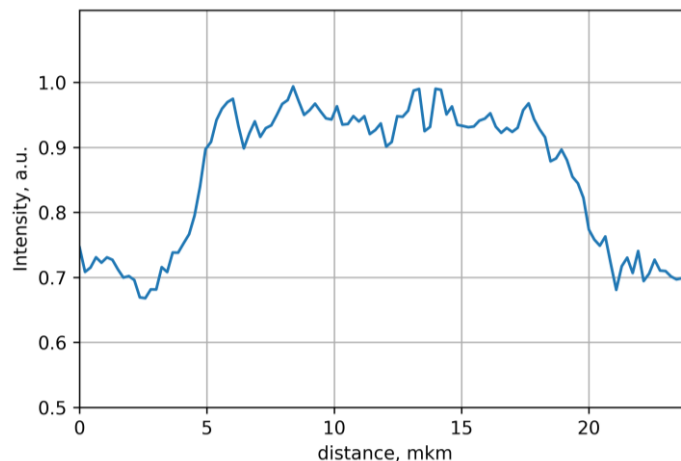


Figure 4. CL profile of the sample recorded at 320 nm across the carbon deposited area.

4. Discussion

CL spectrum of pristine hBN includes peaks in visible range at 1.9 eV and 2.9 eV, which can be attributed to the defects of hBN [5,6,12,13]. The 1.9 eV peak position coincided rather well with the reported previously in [12, 13] for the zero-phonon line of one of two families of single photon sources (1.94 eV). The 2.9 eV peak fall into a spectral region where a broad band centered around 400 nm observed in [14] on hBN powder, which intensity exhibited a drastic reduction under exposure in

oxygen. Narrow 2.9 eV peak similar to the one in our experiment was recently observed in electron irradiated hBN [15], but the microscopic origin of this peak was not discussed. On the other hand, its energy is close to the half of band-gap and might be artefact due to second order diffraction as we did not use any band pass filter in our experiments in order to pick out carbon-related changes in a wide spectral region. Anyway, the intensity of this line was proportional to the sample thickness confirming its bulk origin that allowed to use it as a reference signal to account the light shadowing effect of carbon-rich film formed on the sample surface in the following experiments. More detailed discussion of the origin of these two lines is beyond of the scope of this paper.

The results listed in section 3.1 for the first time showed that local electron beam induced deposition of carbon-rich film onto the surface of hexagonal boron nitride crystal gave rise to the appearance and a drastic increase of a specific ultraviolet luminescence band that exhibits a fine spectral structure consisting of zero phonon line (ZPL) at 4.05 eV accompanied with several phonon replicas. The energy positions of the lines coincide perfectly with the previously reported values for hBN microcrystals grown in molten metals with an addition of graphite [7]. Similar spectral structure was found in ref. [4] on nominally undoped thin hBN flakes.

Besides the series of the narrow spectral lines, we observed a broad line centered at 4.2 eV. Similar band was found in ref. [4], where its intensity also increased after electron irradiation and it was attributed tentatively to some donor-acceptor pairs, formed during electron beam irradiation. Since in our experiments it reduced drastically after oxygen plasma treatment, more probably its source is located immediately on the surface and caused by some volatile substance formed from not completely decomposed hydrocarbons.

The spectral positions of all narrow components of the spectrum in figure 2 perfectly coincide with the reported in [4] values for carbon-related bulk defects. The spectrum in ref. [4] was observed in thin flakes of a thickness of few tens of nanometer prepared by exfoliation and it remained unclear how deep from the surface the defects were situated. In our experiment oxygen plasma treatment at room temperature, conventionally used to transform carbon-related surface contamination to volatile carbon dioxide, did not significantly reduce the carbon-related band intensity. This might serve as an evidence that during electron beam irradiation at the room temperature carbon atoms easily penetrate and become embedded in the hBN lattice forming defects responsible for luminescent band with the ZPL at 4.05 eV.

According to theoretical investigations of the diffusion of interstitial carbon impurity, C_i , in hBN [3] the migration barrier was estimated to be as low as 1 eV, corresponding to a hopping rate to a neighboring equivalent intercalating site of 1 s^{-1} at room temperature. Based on these data, during the annealing at 1000 °C for 30 minutes carbon could diffuse quite so fast that the distribution of carbon interstitials over hBN sample should be homogeneous. However, as one can see from figure 4, enhancement of 4.1 eV band intensity is observed only in the area, where the carbon-rich film was deposited. Thus, we can assume that carbon atoms penetrate into hBN lattice from the surface and form some stable and immobile defects.

On the other side, the defects could be created as a result of electron irradiation. The electron energy used in our experiments is not sufficient for a direct impact creation of the native defects in hBN. However, one can assume that the excitation of electron subsystem plays an important role in the penetration of carbon into the matrix via the mechanisms of recombination enhanced reactions, well known for silicon and other classic semiconductors [16]. Recent report on the formation of new luminescent defect in hBN under the action of 15 keV electrons could serve as evidence of the existence of such processes in hBN as well [15]. In fact, the formation energies of carbon in both types of substitutional position (CN and CB) is noticeably less than hBN band gap [3] making possible their creation in a single non-radiative recombination act of electron-hole pair via electronic levels of a preexisting defect. In this way, most probable, that the defect responsible for the band with the ZPL at 4.05 eV is created near the preexisting defect as the result of the reaction of CN or CB with the latter.

In [10] carbon-oxygen complex ($C_N O_N$) was proposed as a candidate for the carbon-related luminescence centers. This proposition is, however, in contradiction with our results of the impact of oxygen plasma treatment that resulted in a slight decrease of the CL intensity.

In conclusion, we have showed that local electron beam induced deposition of carbon-rich film onto the surface of hexagonal boron nitride at room temperature resulted in the appearance of a bright ultraviolet luminescence due to the creation of carbon-related defects that can serve as single photon sources. The technique can be used for nanofabrication of single photon source devices with desired pattern.

Acknowledgments

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