

## Raman spectroscopy of BN and $B_xN_yC_z$ structures formed in an optical furnace without catalysts

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*Results of Raman spectroscopy investigations of boron nitride (BN) whiskers, BN and  $B_xN_yC_z$  coatings produced in optical furnace without catalysts as well initial h-BN for comparison are presented.*

**Keywords:** *spectroscopy; whiskers; nanotubes; optical furnace.*

Hexagonal boron nitride (h-BN) is iso-structural with graphite and is the normal phase of BN that is stable at room temperature and ambient pressure. It is a wide band gap semiconductor with potential applications in optoelectronic devices. First-principles local-density calculations have shown that the lowest band gap (4,07 eV) is indirect, located near the Brillouin-zone edges. However, due to the quasi-two dimensional nature of the hexagonal structure, the lowest direct band gap is predicted to be close by at 4,2 eV [1]. A wide range of gap energies, such as 5,2 [2] and 5,9 eV [3], have been reported also by experimental studies using various techniques.

Since the applications of BN nanotubes for the making of optical modulators for ultra short laser pulses is one of the promising direction of a science, thereby research of properties of BN and  $B_xN_yC_z$  materials is very important.

It's known that Raman spectroscopy is based on the analysis of inelastically scattered light when the Raman scattering comes from a change in the polarisability of molecules (or atoms). In Raman scattering the modulation of the response by the vibrations play a very important role. The vibrations are Raman active only when the change of the polarizability is induced. The polarizability is changed by the displacement of the atoms during the vibration. This depends on the mechanical deformation induced in the molecule.

The characterization of samples presented in this research was performed with a Dilor spectrometer (XY 800) for Raman scattering in Centre of Photonics and Materials for Prospective Applications (CEPHOMA, Poland). The excitation was induced by a 2 W Argon Laser, 514,5 or 488 nm and 10 nW HeNe, 632,8 nm. DilorXY 800 Spectrograph has motorized xy stage for confocal microscope, 0,1  $\mu\text{m}$  resolution, software for Raman Map.

It was carried out an optical, SEM and TEM investigations of the microstructure and crystallinity of an initial hexagonal boron nitride (h-BN), BN whiskers, and BN and  $B_xN_yC_z$  coatings. Boron nitride whiskers were produced in optical furnace without catalysts on the surface of compacted samples of the initial powders (fig. 1). A quartz chamber was used for the process. Heating of the surface of initial powders was done in a furnace of high intensity optical energy in the flow of dried and purified nitrogen. The optical furnace involves three xenon tubes centered in the focus of the ellipsoidal reflectors. A diameter of the light spot is 10 mm. The calculated value of the density of the light flux energy in the focal zone is about  $E = 0,7 \cdot 10^4 \text{ kW/m}^2$  that

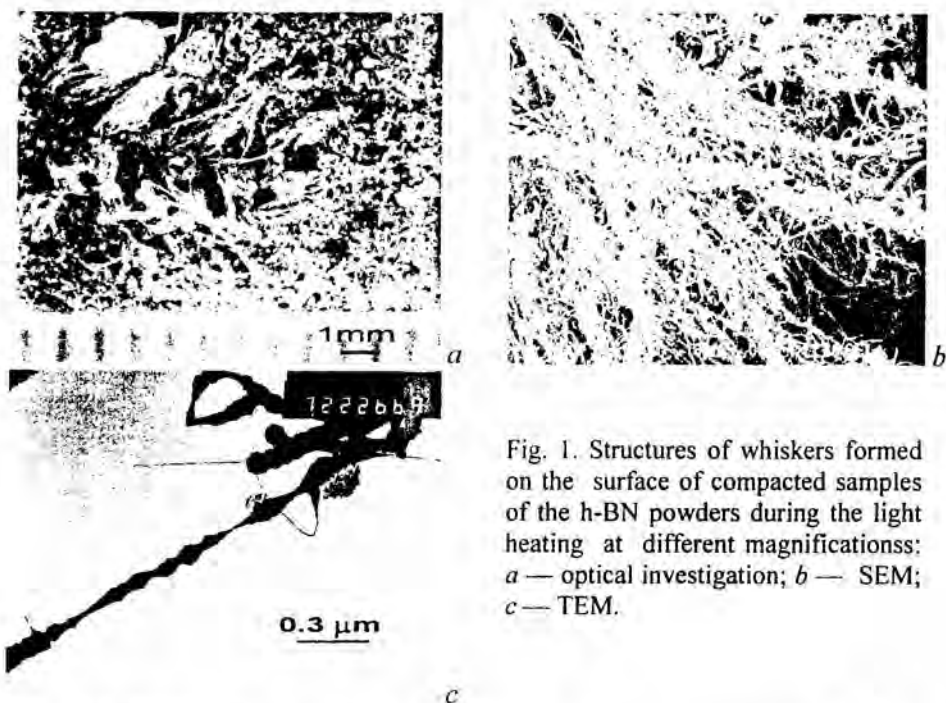


Fig. 1. Structures of whiskers formed on the surface of compacted samples of the h-BN powders during the light heating at different magnifications: *a* — optical investigation; *b* — SEM; *c* — TEM.

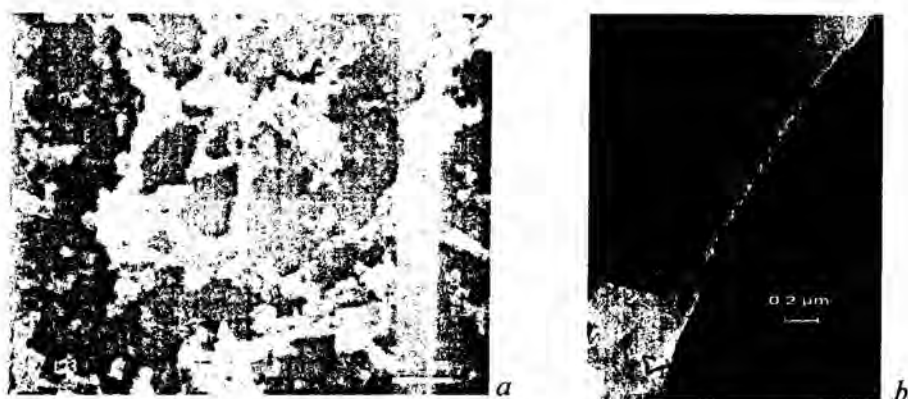


Fig. 2. Structure formed on silicon substrates in the result of deposition h-BN-lamp black composite: SEM (*a*) and TEM (*b*) micrographs.

corresponds  $\sim 2000$  K [3—5]. The coatings were deposited on an unheated silicon substrate by sublimation and evaporation of h-BN and h-BN-lamp black composite in the optical furnace at the density of energy in focal zone set-up  $\sim 0,7 \cdot 10^4$  kW/m<sup>2</sup> (fig. 2).

For comparison, the initial powders of platelet-like fine-grained boron nitride (Chempur, CH070802) have been used. These powders are h-BN textured on 002 with impurity of B<sub>2</sub>O<sub>3</sub>. A diameter of platelets of boron nitride is  $\sim 0,6$ — $1,0$  μm and thickness —  $\sim 0,1$  μm. Detail description of origin powders and experimental presented in work [4].

BN coating consists of hexagonal, two boron-enriched tetragonal phases of BN (B<sub>51,2N</sub> and B<sub>25N</sub>, respectively), tetragonal and rhombohedral phases of pure boron and amorphous phase. B<sub>3</sub>N<sub>5</sub>C<sub>2</sub> coating has more complicated phase composition which is difficult to identify.

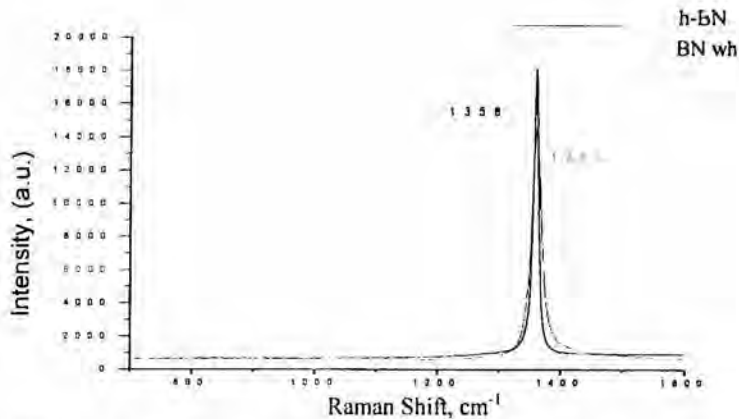


Fig. 3. Raman spectra of h-BN and BN whiskers. The graph shows that the main peak of h-BN near  $1358\text{ cm}^{-1}$  is shifted for BN whiskers.

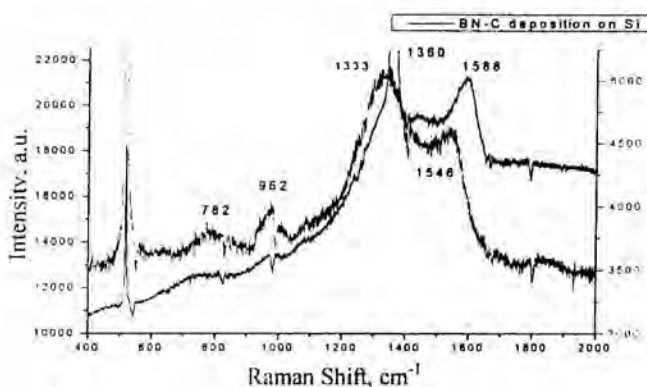


Fig. 4. Raman spectra of  $B_xN_yC_z$  coatings in the different places of a surface of a Si substrate.

The Raman responses for the h-BN, BN whiskers and  $B_xN_yC_z$  coatings are depicted in fig. 3—5.

The dominant peak near  $1360\text{ cm}^{-1}$  that shows up intensely in all samples is attributed to the well known zone-center, counter-phase B—N vibrational mode  $E_{2g}$  within BN sheets (fig. 3—5). A half-width of this peaks for h-BN, BN whiskers, BN and  $B_xN_yC_z$  coatings is 11, 21, 16,  $334\text{ cm}^{-1}$  respectively. Compared to an infinitely long system with periodic boundary conditions like h-BN, the force constant for whiskers could not be reduced because of size effects. Given that the whiskers have a broader size distribution, the force constants which are size dependant will also have a broader distribution, which in turn leads to a larger frequency range (fig. 3). The shift and broadening can be explained in a formulation of the Raman cross section for scattering from nanocrystals in which the wave-vector uncertainty of the phonons is related to the crystal grain size. So, the size of produced BN structures is lower than grain size of initial powders.

As compared to the Raman spectrum of BN whiskers, the  $B_xN_yC_z$  sample shows strong peaks near  $1548$  and  $1588\text{ cm}^{-1}$  (fig. 6). These peaks are clearly due to the  $E_{2g}$  stretch mode of two-dimensional graphite sheet or carbon shells in the  $B_xN_yC_z$  sample [5]. The higher energy of this mode than that of the same

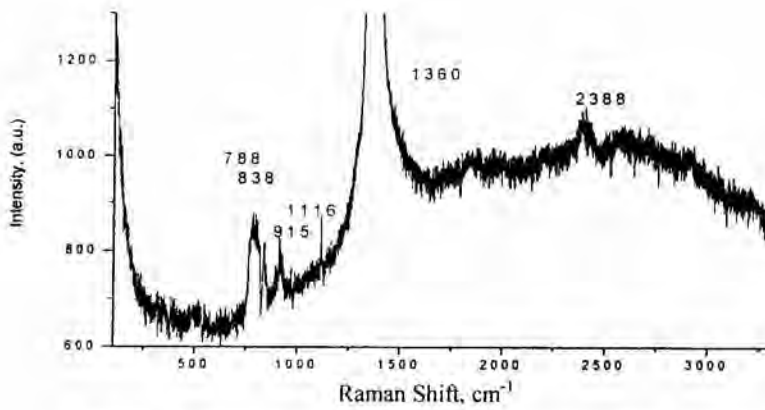


Fig. 5. A detailed analysis of a Raman spectra of BN whiskers.

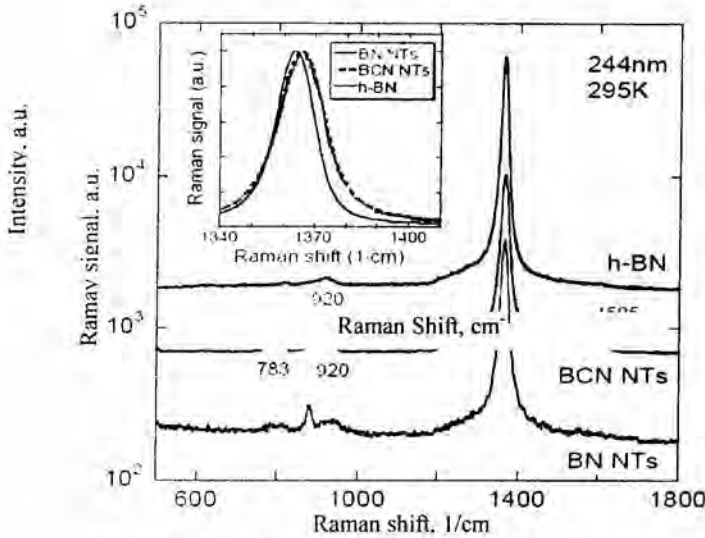


Fig. 6. Raman spectra of h-BN, BN and BCN nanotubes for comparing [5].

mode of BN reflects the softening of the bond as a result of ionicity in BN. The large width may be a result of a superposition of multiple peaks due to differently structured carbon shells, because this mode is chirality and diameter dependent in carbon nanotubes.

It is considered that three absorption frequency regimes for BN nanotubes can be obviously distinguishable at  $\sim 809$ ,  $\sim 1369$  and  $\sim 1545$   $\text{cm}^{-1}$ , although the last is absent for nanotubes in [5].

It follows from a detailed analysis of a Raman spectra of BN whiskers (fig. 5) that the weak absorption at  $\sim 809$   $\text{cm}^{-1}$  is associated with the out-of-plane radial buckling mode where boron and nitrogen atoms are moving radially inward or outward. Supposedly, that the splitting of the radial buckling vibration is related to the complex interaction of buckling vibration at different h-BN sheets that have different diameters and chiralities. However, only highly crystalline BNNTs would show up  $\sim 1545$   $\text{cm}^{-1}$  vibration mode which may shift from sample to sample. This is explained by the change of the average diameter of BNNTs in different samples, attributed to different curvatures of the h-BN

sheets in BNNTs and thus the induced lattice strains along the tangential directions of the nanotubes.

Thus, produced BN whiskers are composed of BN nanotubes with poor crystallinity and  $B_xN_yC_z$  coatings are composed of  $B_xN_yC_z$  nanotubes.

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### **Раманівська спектроскопія BN та $B_xN_yC_z$ структур, сформованих в оптичній печі без каталізаторів**

Л. Л. Сартинська, М. І. Даниленко, Ц. Ястребський

*Представлено результати дослідження Раманівської спектроскопії віскерсів з нітриду бору, BN і  $B_xN_yC_z$  покриттів, отриманих в оптичній печі без каталізаторів, а також вихідного порошку h-BN для порівняння.*

**Ключові слова:** спектроскопія, віскерси, нанотрубки, оптична піч.

### **Рамановская спектроскопия BN и $B_xN_yC_z$ структур, сформированных в оптической печи без катализаторов**

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*Представлены результаты исследования Рамановской спектроскопии вискерсов из нитрида бора, BN и  $B_xN_yC_z$  покрытий, полученных в оптической печи без катализаторов, а также исходного порошка h-BN для сравнения.*

**Ключевые слова:** спектроскопия, вискерсы, нанотрубки, оптическая печь.