JOURNAL OF MATERIALS SCIENCE 28 (1993) 5675–5678

I.r. spectroscopy characterization of various types of structural irregularities in pyrolytic boron nitride

A. S. ROZENBERG, Yu. A. SINENKO, N. V. CHUKANOV
USSR Academy of Sciences Institute of Chemical Physics, 142 432 Chernogolovka, Russia

Samples of pyrolytic BN ceramics were produced by CVD from BCl_3–NH_3–N_2 mixtures at temperatures of 1300–2100 °C, pressures 1–20 torr and varying partial pressures of the components. A theoretical analysis of the dependences of i.r. spectral band frequencies on interlayer distance and crystal block size is given. Five BN structure modifications have been found in BN ceramics from i.r. band shape analysis: hexagonal graphite-like, partially ordered, turbostratic, dense amorphous and highly dispersed amorphous, whose relative content strongly depends on the synthesis conditions.

1. Introduction

Production of coatings and articles of pyrolytic boron nitride (PBN) by chemical vapour deposition (CVD) has recently attained ever-growing importance due to their application to ultra-high-vacuum processes in microelectronics and highly pure chemical processes, which require heat- and corrosion-proof conditions [1, 2] made possible by the peculiarities of the physico-chemical properties of PBN [2].

A successful control over the CVD processes seems to be difficult without preliminary detailed analysis of the dependence of microstructural and kinetic parameters on the synthesis conditions (temperature, partial pressure of the components, the rate of their supply etc.).

The present series of papers concerns the solution of these problems and modelling of the CVD process, taking account of the kinetics of formation and the mutual conversion of structural modifications of PBN.

Physical, mechanical and operational properties of the articles produced are mainly determined by the ratios between the PBN structural components. However, the majority of the experimental methods employed provide averaged characteristics of the material. There are no reliable quantitative methods which could specify the distribution of such structural parameters as the size of crystallites, interlayer distance and distortion of hexagonal layers in the PBN samples.

By means of X-ray analysis and electron microscopy the degree of ordering in BN has been found to vary from three-dimensional (3D) order with a hexagonal layered graphite-like structure (h-BN) to amorphous material (a-BN). An intermediate structural modification of BN is turbostratic boron nitride (t-BN) [5, 6] characterized by only two-dimensional (2D) ordering. Commercial PBN is non-uniform in its structure and contains a number of structural components [5–7] which are likely to result from the complexity of the CVD process, e.g. the presence of several mechanisms of condensed phase formation and growth on the heated surface of deposition [7].

The present paper reports the feasibility of i.r. spectroscopic analysis of the BN structure.

2. Experimental procedure

The method of vacuum CVD was used for PBN sample preparation. PBN was deposited on to a graphite substrate heated by inductive or resistive methods up to 1300–2100 °C. A BCl_3–NH_3–N_2 mixture was fed to a flow-type reactor at variable partial pressures of the components. The total pressure in the reactor was maintained within 1–20 torr.

The PBN samples obtained were compacted with KBr into pellets and their i.r. spectra were registered by means of a Specord-75IR (Germany) at a spectral slit width of $< 1\ \mathrm{cm}^{-1}$.

3. Results and discussion

The vibrational spectra of h-BN with complete 3D ordering and an interlayer distance of 0.333 nm are known [10, 11] to have two bands in the range 400–4000 cm^{-1}. One of these, with the maximum at 1370 cm^{-1}, corresponds to in-plane vibrations (||) and is of an approximately Lorentzian shape with bond asymmetry caused by the boron isotope distribution. The other band at 817 cm (Fig. 1) reflects out-of-plane vibrations (⊥) and is strongly asymmetric, which is mainly caused by violation of the symmetry selection rules [12]. The reason for such violation may be small free path lengths of the corresponding phonons because of anharmonicity.

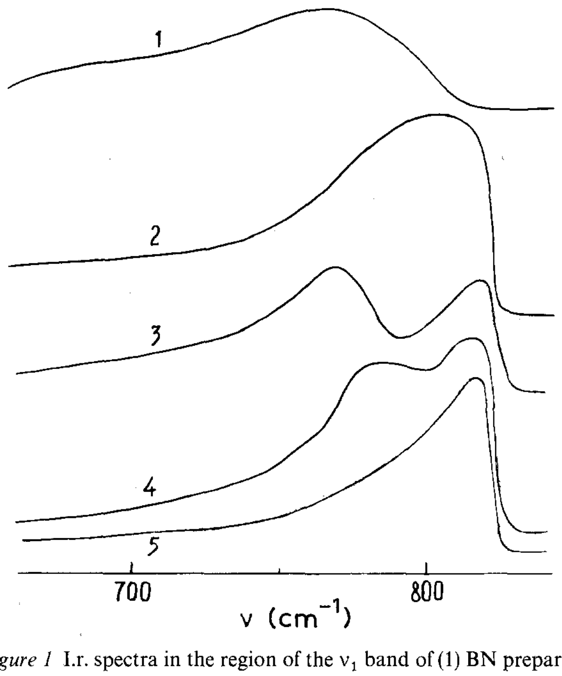

Figure 1 I.r. spectra in the region of the ν_1 band of (1) BN prepared at the cooled reactor wall; ceramics prepared at (2) 1700 °C and 100 torr, (3) 1800 °C and 5 torr and (4) 1800 °C and 20 torr; and (5) pure h-BN.

The i.r. spectra of a typical t-BN with interlayer distance $d_{002} = 0.353$ nm, coherent scattering diameter $L = 3.6$ nm, a narrow distribution of particle size ($\bar{d} = 3.5$ nm) and complete absence of 3D ordering displays broadened bands at 1396 and 800 cm^{-1} [13].

The t-BN band shift into a low-frequency region may be caused by either a decrease in the size of the regular 2D segment within the flat net or an increase in d [12, 13]. Let us consider both in detail.

Kuzuba *et al.* [14] proposed a function including Coulomb and Lennard-Jones terms for the potential energy of interparticle interaction of the BN layers:

$$\varphi(t) = dr^{-6} + \beta r^{-12} + \gamma r^{-1} \qquad (1)$$

The frequency of out-of-plane vibrations is determined by both the rigidity of the layer itself (k) and interlayer interactions of neighbouring layers. Consequently, the effective force constant is d_{002}-dependent according to the following rule:

$$\begin{aligned} k &= k_0 + \Delta k \\ &= k_0 + \frac{d^2}{dq^2}\left[\varphi(d_{002} - q) + \varphi(d_{002} + q)\right]_{q=0}, \qquad (2) \end{aligned}$$

where q is the normal coordinate of the i.r.-active out-of-plane vibrations.

Here we postulate the Kuzuba form for $\beta(d_{002})$ dependence:

$$\varphi(d_{002}) = Ad_{002}^{-6} + Bd_{002}^{-12} + Cd_{002}^{-1} \qquad (3)$$

The coefficients A, B and C can be found from the conditions: $d_{002}^{0} = 0.333$ nm (the interplanar distance of an undistorted lattice), $\varphi(d_{002}^{0}) = -8$ kJ mol^{-1} [14], $\varphi'(d_{002}^{0}) = 0$ (equilibrium condition), $\varphi''(d_{002}^{0}) = 0.516$ mJ cm^{-2} [14].

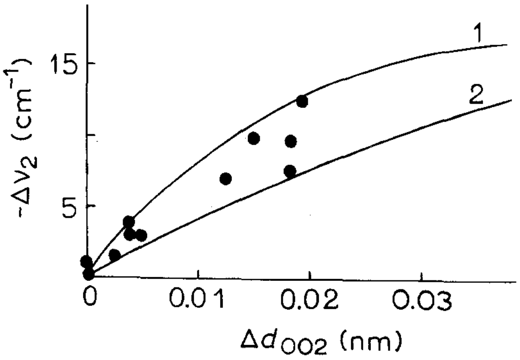

Figure 2 (●) Experimental dependence of $\Delta\nu$ on $\Delta(d_{002})$ and those calculated from the functions of (1) Moore [6] and (2) Kuzuba *et al.* [14] for samples with a homogeneous structure.

The frequency shift caused by the increase in d calculated by taking account of the relation $\nu_{\perp} \simeq k^{1/2}\mu^{1/2}$ (where μ the effective mass of the standard oscillator) is

$$\Delta\nu = \nu_0 - \nu_0\left(1 - \frac{\Delta k}{k_0}\right)^{1/2}$$

By taking a Taylor series expansion for small $\Delta k/k_0$ we obtain the final equation for the frequency shift:

$$\begin{aligned} \Delta\nu = \left(\frac{\nu_0}{2k_0}\right)\frac{d^2}{dq^2}&\left[\varphi(d_{002} - q)\right. \\ &\left. + \varphi(d_{002} + q)\right]_{q=0} \qquad (4) \end{aligned}$$

where $\nu_0 = 817$ cm is the frequency for an ideal crystal of h-BN; the $\varphi(d_{002})$ dependence is given by Equation 3. The Kuzuba form for the $\varphi(d_{002})$ dependence is to be verified. For this purpose the $\Delta\nu(d_{002})$ dependencies were plotted for a model series of samples different in their microstructures [12]. The d_{002} values were determined from the X-ray diffraction data. Besides the experimental dependency of $\Delta\varphi(d_{002})$, those calculated according to the Kuzuba and Moore potential functions are shown in Fig. 2. The experimental points are seen to be approximated by the $\Delta\nu(d_{002})$ dependence calculated from Equation 3. The value calculated from Equations 3 and 4 at $d = 0.353$ nm is equal to 12 cm^{-1}, which is close to the experimentally observed 17 cm^{-1}. The discrepancy of 5 cm^{-1} may arise from the small size of L_a (3.6 nm in this case). Now we can calculate the value of the additional shift of the band due to the finite volume of the 2D regular segment.

Previously it was shown for a one-dimensional periodic structures [15] that the transformation to normal coordinates of the repeating unit allows reduction of the vibrational dynamic problem for the system of n elementary units with r degrees of freedom each to that of the oscillation of r simple chains of n bound oscillators interacting via end oscillators. When expanding this approach, a 2D system of coupled oscillators may be found to correspond to each frequency branch of the lattice.

For a 2D crystal segment of $N \times N$ elementary cells in the approximation of near-neighbour interactions, neglecting boundary effects, the formula for the i.r.-active eigenfrequency belonging to the boundary frequency branch is [16]

$$\nu^2(N) = \nu_0^2 d\cos\left(\frac{\pi}{N+1}\right) \qquad (5)$$

where ν_0 is the frequency of the oscillator in normal coordinates of the elementary cell [15]; d is the width of the eigenvalue zone for out-of-plane vibrations.

As follows from Equation 5, the frequency of a BN particle of 2 nm diameter is 4 cm^{-1} lower than the frequency of an infinite crystal at the same value of d_{002}. The real dispersion surface in the coordinate space "frequency–phase parameter vector components" is steeper in the vicinity of the i.r.-active mode than in the model considered with account taken of near-neighbour interactions only. The real shifts due to the decrease in L_a may therefore be a little greater; however, even in this case its absolute value for t-BN does not exceed 20–25 cm^{-1}.

Thus the band shift of $\nu_\perp$ in t-BN is mainly determined by the increase in d_{002} and to a lesser extent is dependent on the size of the crystalline unit. The maximum shift of the band to the low-frequency region should not appreciably exceed 20 cm^{-1}. However, in the i.r. spectra of PBN obtained at temperatures above 1600 °C there is a band with a maximum within the range 760–790 cm (Fig. 1), its position being dependent on the synthesis conditions. The limiting frequency that corresponds to the infinite value of d_{002} is 800 cm^{-1}; these great shifts may therefore be due only to the presence of an amorphous structural component (a-BN) in PBN with a size of ordered units of the order of 1 nm or less.

A similar amorphous structure was observed by means of electron microscopy in BN films prepared by the method of ionic deposition [4]. It is interesting to note that the presence of an amorphous structural component in the sample is accompanied by the emergence of small shoulders in the i.r. spectrum at 1100 cm^{-1} which may be regarded as coming from groups with sp^3 hybridization. These fragments may be considered as the elements of high pressure structural modifications of BN. When BN samples are annealed at high vacuum at 1600 °C for 24 h the number of these fragments increases (Fig. 3). This process is accompanied by a decrease in the turbostratic component content and nitrogen isolation, the latter being registered by the mass spectrometer. This phenomenon can probably be considered as the formation of sp^3 cross-links between the layers in the least ordered regions of the material.

Besides a dense amorphous structural component, a highly dispersed boron nitride phase, which contains many N–H bonds absorbing in the frequency range from 3100 to 3600 cm^{-1}, is formed as a by-product on the cold wall of the reactor during the synthesis. A ν_1 band in the frequency range from 760 to 790 cm^{-1} (see Fig. 1) rather than a shoulder is a characteristic feature of that phase. There is a small content of a similar structural component in the BN samples prepared at low temperatures.

In the BN samples prepared at high temperatures (above 1700 °C, though this limit depends on some other parameters of the synthesis as will be shown elsewhere) an ordered graphite-like structure predominates with the ν_1 band having the maximum near to 817 cm^{-1} (Fig. 1). The precise position of this maximum may shift into the low-frequency region due to a partial disordering of h-BN that is accompanied by an increase in d_{002}.

Assuming that BN various regions make an additive contribution to the i.r. spectrum we can write the full formula for the spectral band share as follows:

$$\varepsilon(\nu) = \int \rho(x)\,\varepsilon_0(\nu - x)\,dx \qquad (6)$$

where $\rho(x)$ is the frequency probability density of the absorption centers, $\varepsilon_0(\nu)$ is the frequency dependence of the h-BN extinction coefficient and $\varepsilon(\nu)$ is the frequency dependence of the sample extinction coefficient.

By solving the integral Equation 6 for ordered and turbostratic components we can obtain the frequency probability density $\rho(\nu)$ and using the ratio 4 we can obtain the distribution density of the interlayer space (d_{002}). The latter dependence was calculated numerically for a number of BN samples. A typical $\rho(d_{002})$ dependence is shown in Fig. 4. It is seen from the figure that along with h-BN, which has a d_{002} close to a δ-function, and t-BN with a broad distribution of d_{002} in the range of 0.339–0.380 nm, the BN sample contains a component with an intermediate, partially ordered structure and d_{002} in the range from 0.334 to 0.339 nm. It may correspond to a Moore structure of type III [5, 6].

Thus, five BN structure modifications have been found in PBN prepared by the CVD method:

1. Hexagonal graphite-like structure h-BN ($\nu_1^{\max} = 817\ \text{cm}^{-1}$, $L > 100$ nm, $d_{002} = 0.334$ nm).
2. Partially ordered structure po-BN ($\nu_1^{\max} = 814$–$816\ \text{cm}^{-1}$, $d_{002} = 0.334$–0.339 nm).

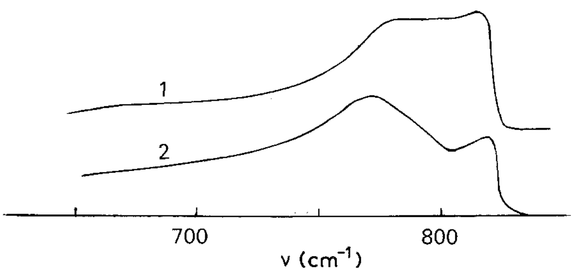

Figure 3 I.r. spectra of samples of BN ceramics synthesized at 1800 °C and a total pressure of 10 torr; (1) initial and (2) after annealing at 1600 °C for 24 h.

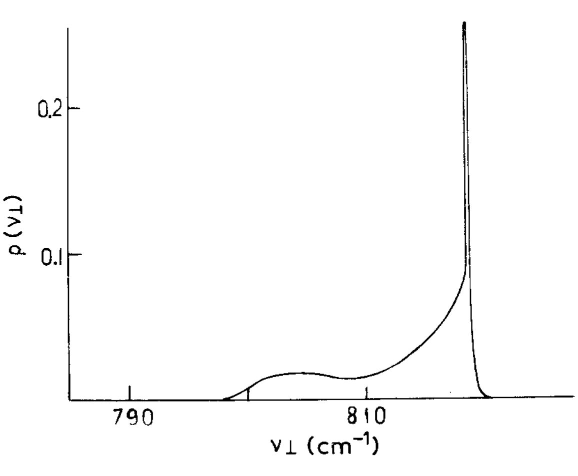

Figure 4 Density of interlayer space distribution in t-, po- and h-BN ceramics synthesized at 1700 °C and a total pressure of 5 torr.

3. Turbostratic structure t-BN ($\nu_1^{max} = 795$–$810\ \mathrm{cm}^{-1}$, $L = 2$–20 nm, $d_{002} > 0.335$ nm).

4. Dense amorphous structure a_1-BN ($\nu_1^{max} = 760$–$790\ \mathrm{cm}^{-1}$, $L < 1$ nm; there is a band at $1100\ \mathrm{cm}^{-1}$ in the i.r. spectrum).

5. Highly dispersed amorphous structure a_2-BN ($\nu_1^{max} = 760$–$790\ \mathrm{cm}^{-1}$, $L < 1$ nm, ν_1 band broad, no band at $1100\ \mathrm{cm}^{-1}$ in the spectrum).

The quantitative determination of amorphous (sum of a_1- and a_2-BN), turbostratic (t-BN) and ordered (sum of h- and po-BN) structural components can be made by means of i.r. spectroscopy using for calibration reference samples [17] with a predominant structure of the same type. The content of BN structural components, as determined by i.r. spectroscopy, gradually changed with variation of the synthesis conditions: 0–35% for amorphous structural components, 0–100% for turbostratic structural components and 0–100% for ordered structural components.

The results of more detailed investigations of the dependence of microstructure on the synthesis conditions of BN ceramics will be given in further papers of this series. It may be noted here that the ratio of the contents of ordered and turbostratic structural components, which were determined by means of i.r. spectral analysis, is in good agreement with similar results which were obtained by means of X-ray phase analysis.

References

1. G. V. SAMSONOV, "Non-metal Nitrides" (in Russian) (Naukova dumka, Kiev, 1969).
2. R. T. PAINE and C. K. NARULA, *Chem. Rev.* **90** (1990) 73.
3. T. MATSUDA, N. UNO, H. NAKAE and T. HIRAI, *J. Mater. Sci.* **21** (1986) 649.
4. D. R. McKENZIE, W. G. SAINTY and D. GREEN, *Mater. Sci. Forum* **54/55** (1990) 193.
5. A. W. MOORE and S. L. STRONG, *Ceram. Eng. Sci. Proc.* **10** (1989) 846.
6. A. W. MOORE, *J. Cryst. Growth* **106** (1990) 6.
7. T. MATSUDA, H. NAKAE and T. HIRAI, *J. Mater. Sci.* **23** (1988) 509.
8. M. BASCHE, *US Patent* 3 152 006 (1964).
9. M. BASCHE and D. SCHIFF, *Mater. Design Eng.* (February 1964) 78.
10. R. J. NEMANICH, S. A. SOLIN, and R. M. MARTIN, *Phys. Rev. B* **23** (1981) 6348.
11. R. GEICK, C. H. PERRY and G. RUPPRECHT, *Phys. Rev II* **146** (1966) 543.
12. V. I. GUDKOVA, A. V. RAJEVSKY, A. S. ROZENBERG and N. V. CHUKANOV, *Surface* (in Russian) No. 8 (1988) 61.
13. V. I. CHUKALIN, N. V. CHUKANOV and S. V. GUROV, *Powder Metall.* (in Russian), No. 1 (1988) 85.
14. T. KUZUBA, T. SATO, T. ISHII and T. ARAI, *Phys. Rev. B: Cond. Matt.* **32** (1985) 1230.
15. A. R. LOGHINOV, V. N. KOZYRENKO, I. D. MIKHILOV, N. V. CHUKANOV and I. V. KUMPANENKO, *Chem. Phys.* **36** (1979) 187.
16. S. F. IPPOLITOVA, I. V. KUMPANENKO, N. V. CHUKANOV and S. G. ENTELIS, *Microchem. Acta* No. 2 (1988) 47.

Received 17 March 1992
and accepted 24 February 1993