Crystallographic aspects related to the high pressure–high temperature phase transformation of boron nitride

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Crystallographic relations between different forms of boron nitride (BN) appearing at the high pressure–high temperature structural phase transformation have been revealed by high-resolution transmission electron microscopy (HRTEM). As starting materials, crystalline hexagonal BN (hBN) with different degrees of crystallinity, or with defects intentionally introduced, were used. Cubic BN (cBN) is formed only as a minor component, the rest consisting of different forms of $sp^2$ bonded BN: hBN, compressed, monoclinic deformed hBN, or turbostratic BN (tBN). The small cBN crystallites (300–400 nm) contain many defects such as twins, stacking faults and nano-inclusions of other BN forms: tBN, rhombohedral BN (rBN) and wurtzite BN (wBN). The cBN phase grows epitaxially on the basal plane of hBN. The nucleation sites for cBN are revealed by HRTEM. They consist of nano-arches ($sp^3$ hybridized, highly curved nanostructures), frequently observed at the edges of the hBN crystallites in the starting materials. Based on HRTEM observations of specimens not fully transformed, a nucleation and growth model for cBN is proposed which is consistent with existing theoretical and experimental models.

1. Introduction

Boron nitride (BN), a man-made compound, has four polymorph forms. Hexagonal BN (hBN), with a structure close to graphite, and rhombohedral BN (rBN) are the less-dense $sp^2$ bonded phases, while hcp BN with a wurtzite structure (wBN) and cubic BN (cBN) with a sphalerite structure are the dense $sp^3$ bonded phases. High pressures (HP) and high temperatures (HT) are needed to transform the less dense phases into the denser ones [1]. Another structural variety of BN, but not a polymorph one, is the turbostratic BN (tBN), which can be described as a highly disordered hBN, by random rotations and translations of the hexagonal planes about the c-axis. Consequently, in tBN the interplanar spacing along the c-axis is variable depending on the degree of disorder and larger than in hBN [2].

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All four polymorph phases of BN have a layered structure with two-fold periodicity for hBN and wBN and three-fold periodicity for rBN and cBN. It is expected that the less dense–dense hBN→wBN and the rBN→cBN transformations will occur by compression, as a result of a displacive, diffusionless structural transition, without breaking the bonds and by preserving the stacking sequence [3, 4]. The energy barrier to activate these transformations is rather small; these transitions are generally rapid.

The (HP HT) hBN→cBN direct transformation is a reconstructive structural transition, with a modification of coordination from 3:3 to 4:4. It occurs at high pressures (P ≥ 6.5 GPa) and high temperatures (T = 1600–2000°C). The transition takes place by breaking the interatomic bonds into structural units and reconstructing the new phase from these structural units. The activation energy of reconstructive transitions is large; the transformation is always assisted by diffusion and consequently it is sluggish. In our particular case, hBN has very strong covalent bonds with sp³ hybridisation in the hexagonal (graphitic) planes, and weak van der Waals bonds between these planes, while cBN has only covalent (partially ionic) bonds, with tetrahedral three-dimensional sp³ hybridisation [5].

For industrial applications, a catalytic conversion of hBN to cBN at less severe conditions (P = 1–6 GPa, T = 1400–1600°C) is performed [6]. The transformation occurs in the liquid phase, by melting followed by precipitation in a catalytic flux. Recently it has been shown that it is possible to reduce the temperature of the direct transformation hBN→cBN. This is done by mechanically milling the hBN precursor, in order to introduce defects [7], or even to transform the starting material into nanocrystalline or amorphous BN [8], before its conversion to cBN. At pressures of 7.7 GPa and temperatures as low as 1200°C [4] or 900°C [8], cBN starts to form.

It appears that pressure and temperature are not the only factors which determine the mechanism and kinetics of the direct transformation process. The physical properties of the starting material as well as the degree of crystal perfection, the degree of dispersion, or the presence of impurities should also be taken into consideration [6,8].

In this paper, we present a crystallographic study of the HP HT hBN→cBN direct transformation, as revealed by high-resolution transmission electron microscopy (HRTEM). The influence of the microstructure of the hBN precursor on the nucleation of the cBN phase is also investigated.

2. Structural considerations

A simple structural relationship exists between the four polymorphs of BN [3, 4, 9–12]. The structure of hBN [13] consists of hexagonal planes of boron and nitrogen, stacked along the c-axis of the hexagonal prism in the sequence AA’ AA’, etc. B and N atoms occupy alternate positions in the vertices of the hexagons as well as along the c-direction. The lattice parameters of hBN are \(a = 0.2502\) nm, \(c = 0.666\) nm. The rBN structure is similar to that of hBN; it is also formed by the stacking of hexagonal BN planes, but the stacking sequence is ABC, ABC, etc. [14]. The lattice parameters of rBN, referred to as the hexagonal system, are \(a = 0.2504\) nm, \(c = 1.0\) nm.

By applying a high pressure to hBN or rBN, they transform to denser forms of BN, i.e. to wBN and cBN, respectively. Upon compression of hBN, two effects occur: a reduction of the interplanar spacing along the c-axis and a deformation of
the flat hexagonal BN planes by splitting into two planes, one of boron atoms the other of nitrogen atoms, giving rise to the hexagonal corrugated or puckered planes of wBN [3, 11]. The lattice parameters of wBN are \( a = 0.2550 \text{ nm}, c = 0.4254 \text{ nm} \). Similarly, the cBN structure is also built up from corrugated hexagonal planes stacked along the (111) direction of the cube. The transformation can occur directly by compression of rBN and puckering of the hexagonal planes [3]. The lattice parameter of cBN is \( a = 0.3616 \text{ nm} \).

The following crystallographic relations exist between the parent and transformed phases:

\[
\begin{align*}
(0002)_h/(0002)_w, & \quad [2\bar{1}10]_h/[2\bar{1}10]_w, \text{ for } hBN \rightarrow wBN, \\
(0003)_h/(1\bar{1}10)_w, & \quad [2\bar{1}10]_h/[\bar{1}1\bar{1}0]_w, \text{ for } rBN \rightarrow cBN.
\end{align*}
\]

The hBN→cBN transformation being a reconstructive one, bonds have to be broken and reconstructed. Nevertheless, there is a preferential epitaxial relationship between the two crystalline phases [10, 15, 16]. Both the \{111\} planes of cBN and the \{0002\} hexagonal planes of hBN are constituted by hexagons of B and N atoms in alternate positions. The B–N bond length in the (111) projection of the cBN structure is 0.1485 nm, while the corresponding distance in the hexagonal plane of hBN is 0.1440 nm, showing a rather good match between the interatomic distances in the close packed planes. Moreover, since the distance between the (0002) hexagonal planes in hBN is 0.333 nm and the distance between the (111) planes in cBN is 0.209 nm, they approach the 2:3 ratio, fairly close to the ratio between their densities (2.27 g/cm\(^3\) for hBN and 3.5 g/cm\(^3\) for cBN). According to Widany et al. [10, 16], this allows for a low strain well-bonded interface between both structures: three (111) layers in cBN should match two layers of hBN and form a semi-coherent interface. The crystallographic relation of the mutual orientation of both phases is:

\[
(0002)_h/(1\bar{1}10)_w \text{ and } [2\bar{1}10]_h/[\bar{1}1\bar{1}0]_w.
\]

3. Experimental

Two different types of commercial crystalline hBN were used as starting material, one showing a high degree of order along the c-axis and the other being less ordered. We will note them H1 and H2, respectively. The well-crystallized H1 sample had large grains, with an average diameter of 1600 nm, while for sample H2, the average grain size was 300 nm.

A part of the H1 sample was mechanically ball-milled for 15 minutes at room temperature to ease the experimental conditions for the cBN conversion [7]. Sample H2 was not subjected to mechanical milling.

The HP HT synthesis experiments were performed using H1 powders (as received), H1 powders (ball milled) and H2 powders. A straight-bore, high-pressure Belt apparatus was used to induce the transformation. Since our aim was to perform a microstructural study of the direct transformation, the specimens were prepared in conditions of pressure and temperature at which the transformation was not complete and both the parent and transformed phases coexist. Table 1 gives the experimental conditions for sample preparations.

HRTEM studies were performed with a JEOL 4000 EX electron microscope. TEM samples were prepared by dispersing the powders ultrasonically in ethanol and depositing a drop of the colloid on a holey carbon grid.
Table 1. Experimental synthesis conditions for the samples used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>hBN starting material</th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>t (min.)</th>
<th>Formation of cBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>H1</td>
<td>6</td>
<td>1450</td>
<td>15</td>
<td>No</td>
</tr>
<tr>
<td>A2</td>
<td>H1</td>
<td>6</td>
<td>1650</td>
<td>15</td>
<td>Yes</td>
</tr>
<tr>
<td>A3</td>
<td>H1</td>
<td>7</td>
<td>1450</td>
<td>15</td>
<td>Yes</td>
</tr>
<tr>
<td>B1</td>
<td>H1 ball milled</td>
<td>6</td>
<td>1450</td>
<td>15</td>
<td>Yes</td>
</tr>
<tr>
<td>B2</td>
<td>H1 ball milled</td>
<td>6</td>
<td>1650</td>
<td>15</td>
<td>Yes</td>
</tr>
<tr>
<td>B3</td>
<td>H1 ball milled</td>
<td>7</td>
<td>1450</td>
<td>15</td>
<td>Yes</td>
</tr>
<tr>
<td>C1</td>
<td>H2</td>
<td>6.5</td>
<td>1450</td>
<td>15</td>
<td>No</td>
</tr>
<tr>
<td>C2</td>
<td>H2</td>
<td>6.5</td>
<td>1650</td>
<td>15</td>
<td>No</td>
</tr>
</tbody>
</table>

4. Results and discussion

4.1. The microstructure of the hBN starting materials

Figure 1a is a characteristic HRTEM image along the [2110] zone axis of an hBN crystallite from sample H1, not subjected to mechanical milling. An almost perfect stacking of the hexagonal planes with very few stacking faults, characteristic of well crystallized hBN, is evidenced. Figure 1b on the other hand shows the HRTEM image of a crystallite from sample H2. In this case, the stacking along the c-axis is disordered. The image reveals small regions (2–3 nm wide) where lattice fringes in both directions were present, alternating with zones with a modified contrast. In these zones the hexagonal planes are slightly rotated about the c-axis, which explains the loss of contrast along them. The hexagonal planes are also randomly translated over a distance equal to \( c/2[0002] \). A large number of irregular stacking faults bordered by dislocations with Burgers vector \( c/2[0002] \) are present [17]. Some of these dislocations are marked by arrows in figure 1b.

The [2110] HRTEM images of the edges of the sample H1 reveal a very interesting phenomenon. In figure 2, a 180° curving of the graphitic sheets at the crystallite edge can be observed. The (0002) hexagonal planes bend back and join in pairs, forming nanoarches at the edges of the hBN crystallites. In most of the cases, these nanoarches have triple layer walls. The formation of similar nanostructures was obtained by very intense electron beam irradiation [18] and by laser pyrolysis of turbostratic BN, followed by a heat treatment at 1400–1650°C in nitrogen to transform the tBN into hBN [19]. The process is assumed to take place in order to minimize the number of dangling bonds at the border of the hexagonal layers. In our case, such nanoarches have been observed on the edges of crystallites from different hBN samples, of different provenances and by no means were they produced while examining the material in the electron microscope. Moreover, it has been observed that prolonged exposure to the electron beam, in normal conditions of HRTEM, destroys the nanoarches and transforms them into amorphous BN.

Because of the high density of nanoarches at the edges of the crystallites, H1 has been chosen as starting material to induce the direct transformation to cBN. It should also be noted that sample H2 did not show nanoarches.

The formation of nanoarches at the edges of the crystallites in some of the hBN specimens should not be surprising. In the process of thermochemical
Figure 1. [2110] HRTEM images of the hBN samples used as starting material to induce the HP HT transformation to cBN: (a) well-crystallized sample H1, without mechanical milling; (b) sample H2 with defects; dislocations with Burgers vector $\mathbf{b} = \frac{c}{2}[000\bar{2}]$ are marked with arrows.

Figure 2. Characteristic HRTEM images along [2110] for an hBN crystallite from sample H1 showing the presence of nanoranches at the edge.
synthesis of hBN, the first product obtained is turbostratic BN [20]. A crystallization process of tBN, called graphitization [2], is realized at temperatures between 1600 and 2000°C, in several heating cycles. The graphitization process occurs by parallel alignment of the hexagonal planes and reduction of their interplanar distance from 0.36 - 0.34 nm, as it is in tBN with different degrees of three-dimensional order, to 0.333 nm as in hBN. Since the graphitization process takes place at rather high temperatures, depending on the conditions in which it develops, the formation of nanoarches at the edges of crystallites in certain hBN samples could be possible. It is also worth mentioning that similar curved BN nanostructures were observed in BN thin films, in the presence of hBN/tBN or rBN/tBN phases [9, 21].

4.2. Structural aspects related to the hBN→cBN transformation: identification of the nucleation sites for cBN

The pressure and temperature at which our material was produced is below the values at which cBN is formed by direct transformation according to the BN phase diagram [1]. Consequently, in specimens of type A or B (see table 1), for which we used hBN H1 as starting material, cBN crystals are formed only as a minor component, the rest of the specimens consisting of hBN-like phases, while in C-type specimens (table 1), synthesized from hBN H2, cBN is not observed. At first sight, this seems to be in contradiction with other results ([6] and references therein). As a matter of fact, in the conditions of rather low pressures used in our experiments (6 - 7 GPa), it has been shown that cBN can be formed by direct transition only if the starting material is in the turbostratic or even in the amorphous BN phase, but not in the crystalline hBN, as in our case for H2. We will see further that this is a general statement which has to be revised if nucleation centres for cBN already exist in the starting material.

In the C-type specimens subjected to 6.5 GPa and temperatures of 1450 or 1650°C, we observed only structural modifications of the hBN phase; i.e. an increase of the crystallite perfection along the c-axis and a clear tendency of curving of the hexagonal planes with sometimes the formation of nanoarches. This effect of bending of the graphitic planes in hBN subjected to HP HT is illustrated in figure 3,

![Figure 3](image)

Figure 3. Local folding of an hBN crystallite after HP HT treatment (sample C1). In the folded region tBN is formed (arrow).
which is a HRTEM image of specimen C1 close to the [2\overline{1}10] zone axis. In this figure, in comparison with figure 1a at the same magnification, the interplanar distance between the bent planes (indicated with an arrow) is 0.35\,\text{nm}, larger than the interplanar spacing of the basal planes in hBN (0.33\,\text{nm}, used as calibration). In the regions with bent planes, turbostratic BN is formed. It is worth mentioning that both C1 and C2 samples showed a rather high density of such curved nano-structures of BN, which proves that they are formed in crystalline hBN subjected to HP HT. The formation of similar bent structures has already been evidenced for hBN subjected to 7.7\,\text{GPa} and 1800\,\text{C} for 20\,\text{min} [22]. Besides cBN as a minor component, the authors observed the formation of curved nano-structures at the edges of the untransformed hBN crystals. In these regions tBN has been identified.

Figure 4 is a HRTEM image of sample C2 taken along the [2\overline{1}10] zone axis of hBN. Two aspects should draw our attention: the bending of the lattice planes with the formation of a nanoarch and the fact that the arrays of white dots do not form rectangles, as it should be in hBN (see figure 1a for comparison). The distortion angle is approximately 5\,\text{°}. This means that the crystalline symmetry is no longer hexagonal, the crystal being deformed towards a monoclinic structure [23]. This monoclinic form of BN, obtained by compression of hBN at high temperature has been termed 'compressed hBN' by Horiiuchi et al. [23] who determined the following lattice parameters for monoclinic BN: \(a_m=0.433\,\text{nm}, b_m=0.250\,\text{nm}, c_m=0.31-0.33\,\text{nm}, \beta=92-95\,\text{°}\), the \(b_m\) axis being parallel to the \(a\)-axis of hBN. In figure 4, the interplanar distance measured along the \(c\)-axis is 0.32\,\text{nm}, smaller than in hBN, but similar to the value in monoclinic deformed BN or compressed hBN. Dislocations, with Burgers vector \(c/2[001]\), are also present in figure 4; they are marked by arrow heads.

TEM studies show that in all the materials where cBN has been formed, the crystallites are rather small (300-500\,\text{nm}) and have no well-defined shapes. Although the preparation conditions for the A- and B-type specimens are similar (see table 1), in the A-type specimens, synthesised from hBN H1 not subjected to ball milling, the cBN crystals are less often observed than in the B-type specimens produced.

Figure 4. HRTEM image of sample C2 along [2\overline{1}10]_{hBN}. After compression to 6.5\,\text{GPa} and heating at 1650\,\text{C} the hBN crystallite is deformed to a monoclinic BN (distortion angle of \(\sim 5\,\text{°}\)) and a nanoarch is formed. Dislocations with Burgers vector \(b=c/2[001]\) are marked with arrowheads.
from hBN H1 mechanically milled. In all cases, cBN remains the minor component. In specimen A1, produced at the lowest pressure and temperature from a well-crystallized hBN, not subjected to ball milling, no cBN crystallites are observed. These results confirm that the intentional introduction of defects in the well-crystallized hBN starting material lowers the pressure and temperature conditions for which cBN is formed by direct transformation.

Comparing samples A2 and A3, produced from hBN with nanocrystals at the grain edges, with samples C1 and C2, synthesised in similar conditions, but from hBN without nanocrystals, the hBN→cBN transformation is definitely favoured by the presence of the nanocrystals, regardless of the degree of crystallization or the existence of defects in the starting material. The appearance of curved nanostructures in samples where the hBN→cBN transformation took place also confirms this assumption. Figure 5 is a HRTEM image of specimen A3 along the [110] zone axis of cBN. It reveals the interface between a cBN crystallite and a hBN crystallite where the (111) planes of cBN are an extension of the bent hBN (0002) basal planes of a nanocrystal. In the transient zone, there is a clear orientation relationship between the two structures of BN in the sense that (0002)h//(111)c and [2110]h//[110]c. The hBN crystallite is 'compressed' showing a slight monoclinic deformation of approximately 2° [23]. Away from this transient zone, curved and disordered BN nanocrystallites are present. The interplanar spacing measured between the bent planes is 0.35 nm, as in tBN.

Figure 6 is a typical HRTEM image for a sample which was only partially transformed. The cBN crystallite is surrounded by a rather extended zone in which different curved and disordered nanocrystalline forms of turbostratic or compressed hBN, randomly oriented to each other, are present. All these disordered hBN forms probably constitute debris of the starting material (highly crystalline hBN) which has been broken up at the transition [24]. The direct transformation hBN→cBN, being a solid state reconstructive transition between two phases with very different structures and volumes, is accompanied by a fragmentation of the parent phase in nanometre-sized disordered domains. As a result of the applied high pressure, turbostratic and compressed hBN are formed as transient products.
as has been also observed by Horiuchi et al. [23]. Once formed, the cBN nuclei grow at the expense of the disordered BN which surrounds it, and through which atoms can diffuse more easily in order to build up the new phase. This disordered material would disappear when the transformation is completed.

The transformation takes place in all B-type specimens (table 1), even in B1 which is produced at the lowest temperature and pressure. Moreover, we find more frequently cBN crystallites in the B-type than in the A-type specimens. This confirms the results of Horiuchi et al. [7], where it was shown that the conditions in which the direct transformation occurs can be favoured by a mechanical milling of the starting material to introduce defects. However, this contradicts our own results on the C-type specimens, produced from an hBN precursor with defects. The difference is the presence of the nanoarches in hBN H1 as compared with hBN H2 starting materials. This aspect favours the fact that nanoarches can constitute nucleation sites for cBN.

The influence of nanoarches on the nucleation of cBN has been studied by Collazo-Davila et al. [25] for cBN thin films. In this paper, the authors suppose that nanoarches are formed in the hBN layer, in the initial stages of the deposition process, as a result of the strain induced by the ion bombardment. The formation of nanoarches decreases the total surface energy of hBN by saturating the dangling bonds, but, on the other hand, the bending of the basal $sp^2$ bonded planes increases.

![Figure 6. HRTEM image of a cBN crystallite and the zone surrounding it, revealing the fragments of disordered metastable forms of BN appearing in the transient stage of the transformation: tBN, compressed hBN (arrowed) and curved nanostructures. Moiré contrast from overlain $sp^2$ material can also be observed.](image)
the strain energy in the bonds. The authors claim that the bond strain in the nanoarches lowers the energy barrier for the sp$^3$ hybridisation [25]. By diffusion of B and N atoms to the arches with the formation of sp$^3$ bonds, the strain energy in the bonds is released and the arches open. As the diffusion process continues the sp$^3$ bonded network increases till the cBN nuclei are formed.

All our results confirm that the nanoarches at the edges of the hBN crystallites indeed constitute nucleation sites for cBN. Moreover, these highly curved BN nanostructures can be produced in hBN powders were they were initially not present, by subjecting them to HP HT conditions. It is very likely that in the initial stages of the HP HT hBN \( \rightarrow \) cBN transformation, the bending of the hexagonal planes at the edges of the hBN crystallites will induce some degree of sp$^3$ hybridisation of the bonds [18, 25–28], with the formation of sp$^3$ hybridized structural units. These structural units will constitute the nucleation centres for cBN.

Density-functional based tight-binding calculations on the stability of the hBN/cBN interface [10, 16] predict a preferential geometric and epitaxial relation between the (1010) prism plane of hBN and the (112) plane of cBN. Moreover, we have found that there is a strong similarity between the basal (0002) planes in hBN and the (111)-type planes in cBN. Three (111) planes of cBN match almost perfectly two (0002) planes of hBN. The mismatch of approximately 5% is taken up by hBN, which has a large compressibility along the c-axis. Because of the similarity between both structures, cBN will preferentially nucleate on the prism planes of hBN, i.e. on the edges of the hBN crystallites, where nanoarches can exist.

According to Widany et al. [10, 16], the epitaxial relation between hBN and cBN is (0002)$_h$/[(111)$_c$], and [2110]$_h$/[1110]$_c$; this is confirmed in figure 7. The 2:3 matching between the (0002) planes of hBN and the (111) planes of cBN is revealed by the continuous connection between the basal planes of hBN and a set of the (111) planes of cBN. The interface is semi coherent because on the edge of the cBN crystal, free (111) planes with dangling bonds exist.

4.3. Microstructure of cBN resulting from the incomplete transformation

HRTEM reveals structural defects in all cBN crystallites formed by the HP HT direct transformation under the conditions given in table 1. The most frequently observed defects are twins and stacking faults, but also nanoarches of other BN

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Figure 7. HRTEM image showing the epitaxial growth of cBN on the hBN prism plane. The 2:3 matching between the (0002) planes of hBN and the (111) planes of cBN is revealed.
forms are encountered. Figure 8a is a HRTEM image of a region in a cBN crystal in which other forms of BN are revealed. In the slab traversing the image, different types of graphitic BN are present. In very restricted zones such as those marked with thick arrows, rhombohedral BN can be identified. The fast Fourier transform (FFT) corresponding to one of these zones (figure 8b) can be indexed as the rhombohedral BN structure, with lattice parameters $a = 0.2504 \text{ nm}$ and $c = 1.0 \text{ nm}$, along the [2110] zone axis. In this orientation of the rBN phase, the epitaxial relations $(0003)_r//[(111)_{c}$, [2110]$_r//[110]_{c}$, between rBN and cBN should hold, because the spacing between the basal planes in rBN is $0.333 \text{ nm}$ as it is in hBN. But, in this particular case, since the $(0003)$ planes of the rBN phase in the slab are not oriented parallel with the $(111)$ planes of the cBN crystal, they bend towards both sides of the slab in opposite senses so that, at the edges of the slab, they match the $(111)$ planes of cBN in the ratio $2.3$. The rBN domains are all nanometre size. The curving of basal planes results, as in the case of hBN, in the coexistence of rBN and tBN phases. This has also been observed in BN thin films [9, 12, 15, 21].

The extended defect in the left part of figure 8a that intersects the slab is enlarged in figure 8c. The contrast is similar to a wurtzitic BN phase oriented along [2110].

Figure 8. (a) HRTEM image of a cBN crystal containing different deviations from perfection: nanodomains of rBN, and stacking errors of the wBN type; (b) FFT of an rBN nanodomain, which can be indexed with the rBN structure along the [2110] zone axis; (c) Experimental (right) and simulated image (left) of a wBN stacking error inserted in the cBN crystal. The simulation is for a defocus of $-40 \text{ nm}$ and a thickness of $2.6 \text{ nm}$. The orientation relation between wBN and cBN used for the simulation are: $(0002)_w//[111]_c$ and [2110]$_w//[110]_c$. 
The thickness of this defect is equal to one unit cell of wBN along the $a$-direction. Image simulations were performed using the Mac Tempus programme, for a wBN slab, inserted in a cBN crystal. The following orientation relations between wBN and cBN were considered: (0002)$_s$//[(111)$_c$ and [2110]$_s$//[110]$_c$. The simulated image for a defocus value of $-40$ nm and a thickness of 2.6 nm is inserted in figure 8b. wBN were only found very occasionally and they can be considered as defects in the cBN stacking.

Figure 9a is an image of a cBN crystallite in sample B3 revealing a defect frequently observed in the cBN samples produced at lower temperatures. It consists of a slab of turbostratic BN inside a cBN crystal and ending at its surface, with the hexagonal planes of tBN more or less aligned with the (111) planes of cBN. After 5 minutes of exposure to the electron beam in the microscope, in normal working conditions for HRTEM, the image changes to the one in figure 9b. The defect has widened, as a reverse transformation cBN$\rightarrow$tBN takes place under electron irradiation at 400 kV. Sachdev et al. [29] have shown that the cBN$\rightarrow$hBN phase transition is possible at normal pressure. The temperature at which the transformation starts, as observed by DTA measurements is 900°C, for a cBN sample with crystallites with average dimensions of 1000 nm. It was also shown by Sachdev et al. [29] that the onset temperature for the phase conversion is lower if the cBN crystallite dimensions
are lower. In our case, the dimensions of the cBN crystallites are on average three times smaller and already contain a slab of metastable turbostratic BN. As figure 9b shows, the material that results from the cBN → hBN transformation is a rather disordered graphitic BN, but with a clear tendency to align the basal planes with one of the (111)-type planes of the cBN crystal.

5. Conclusions

During the HP HT phase transformation of hBN, the following crystallographic relations between different forms of BN have been revealed:

\[
(0002)_h//\langle 111 \rangle_c \quad \text{and} \quad [2\overline{1}0]_h//[\overline{1}10]_c
\]
\[
(0003)_h//\langle 111 \rangle_c \quad \text{and} \quad [2\overline{1}0]_h//[\overline{1}10]_c
\]
\[
(0002)_h//\langle \overline{1}1\overline{1} \rangle_c \quad \text{and} \quad [2\overline{1}0]_h//[\overline{1}10]_c
\]

As theoretically predicted, cubic BN, grows epitaxially on the prism planes of hexagonal BN. HRTEM evidences a continuous connection between the basal planes of hBN and the (111) planes of cBN: three (111) layers in cBN match two (0002) layers in hBN. The interface is semi coherent, because on the edge of the cBN crystal free (111) planes with dangling bonds exists. HRTEM results confirm the stability of this predicted cBN/hBN interface.

The nucleation sites for cBN consist of \(sp^3\) hybridized nanoarches at the edges of the hBN crystallites in the starting material. These highly curved BN nanostructures can be produced in the hBN powders by compression at high temperatures. It is very likely that in the initial stages of the hBN → cBN transformation, the bending of the hexagonal planes lowers the barrier for \(sp^3\) hybridisation, favouring the formation of the \(sp^3\) hybridised structural units. As more B and N atoms diffuse to these \(sp^3\) hybridised structural units, cBN nuclei are formed.

The hBN → cBN direct transformation being of the reconstructive type, is accompanied by a fragmentation of the parent phase in nanometre-size disordered domains. HRTEM of the partially transformed samples reveals that besides the highly curved BN nanostructures, turbostratic and compressed BN appear in the regions surrounding the cBN crystallites. Once the cBN nuclei formed, they may further grow at the expense of the disordered BN surrounding them.

Rhombohedral BN and wurtzite BN are present only as nanometer size inclusions in the cBN crystals formed in the partially transformed specimens.

Turbostratic BN is frequently observed as inclusion slabs in the cBN crystallites produced at lower temperatures. Exposed to the electron beam during HRTEM, these tBN slabs widen, indicating a cBN → tBN reverse transformation under the 400 kV electron irradiation. The resulting material is a rather disordered hBN with a clear tendency for aligning its basal planes with one of the (111) planes of cBN.

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References