Growth and structure of prismatic boron nitride nanorods

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Prismatic boron nitride nanorods have been grown on single crystal silicon substrates by mechanical ball-milling followed by annealing at 1300 °C. Growth takes place by rapid surface diffusion of BN molecules, and follows heterogeneous nucleation at catalytic particles of an Fe/Si alloy. Lattice imaging transmission electron microscopy studies reveal a central axial row of rather small truncated pyramidal nanovoids on each nanorod, surrounded by three basal planar BN domains which, with successive deposition of epitaxial layers adapt to the void geometry by crystallographic faceting. The bulk strain in the nanorods is taken up by the presence of what appear to be simple nanostacking faults in the external, near-surface domains which, like the nanovoids are regularly repetitive along the nanorod length. Growth terminates with a clear cuneiform tip for each nanorod. Lateral nanorod dimensions are essentially determined by the size of the catalytic particle, which remains as a foundation essentially responsible for base growth. Growth, structure, and dominating facets are shown to be consistent with a system which seeks lowest bulk and surface energies according to the well-known thermodynamics of the capillarity of solids.

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I. INTRODUCTION

The introduction of nonhexagonal atomic rings into a formerly two-dimensional hexagonal network of \(sp^2\)-bonded carbon atoms means that three-dimensional networks and repetitive atomic systems other than simple crystals can be experimentally constructed.1 Certainly the best known and most symmetrical such structure is fullerene—the \(C_{60}\) molecule—which has a closed truncated icosahedral geometry \((I_h)\), and where overall positive Gaussian curvature is a consequence of 12 pentagons embedded symmetrically into a parent twenty-hexagon mesh.2 Various carbon nanostructures can be similarly constructed, including nanorods or nanobelts,3 nanotubes,4 nanocones,5 and bamboo-like hollow structures.6

Hexagonal boron nitride (hBN) is an isoelectronic molecular analogue of graphitic carbon, and BN nanostructures also exhibit diverse morphologies.7–13 Those with a cuneiform internal atomic arrangement are of particular interest. Not only do they promise specific physical properties directly associated with their unique structure14,15 but a knowledge of the dynamics of their assembly can be of critical importance in understanding the physical processes of nucleation and growth of curved carbon or BN structures generally, and especially for nanotubes themselves.1,5 In this paper we report and discuss experiments on the structure and growth mechanism of prismatic boron nitride nanorods, grown via a mechanical ball-milling and annealing method described previously.16,17

II. EXPERIMENT

The intention from the outset was to attempt to grow boron nitride nanorods by means of heterogeneous nucleation, which is by catalysis using iron, on a single crystal silicon base. In each experimental run, therefore, a thin layer of iron nitrate (from its methanol solution) was deposited onto a clean \{100\} oriented silicon substrate, which was in turn rested horizontally on mechanically ball-milled \(B_4C\) powder in direct contact with the silicon surface treated with the iron nitrate. Each such module was preheated at 500 °C for 1 hour and annealed at 1300 °C for 8 hours in an alumina tube in a nitrogen flow of 1400 ml/min. Additional growth details are described elsewhere.16,17 The chemical reaction pathways leading to boron nitride supply are essentially as follows.

(i) Decomposition of iron nitrate:

\[
4\text{Fe(NO}_3\text{)}_3(s) = 2\text{Fe}_2\text{O}_3(s) + 12\text{NO}_2(g) + 3\text{O}_2(g). \tag{1}
\]

(ii) Reduction of iron oxide:

\[
\text{Fe}_2\text{O}_3(s) + 3\text{Si}(s) = \text{Fe}_3\text{Si}(s) + 2\text{SiO}_2(s). \tag{2}
\]

\[
3\text{Fe}_2\text{O}_3(s) + 11\text{Si}(s) = 2\text{Fe}_3\text{Si}(s) + 9\text{SiO}_2(s). \tag{3}
\]

(iii) Formation of boron nitride:

\[
\text{B}_4\text{C}(s) + 2\text{N}_2(g) = 4\text{BN}(s) + \text{C}(s). \tag{4}
\]

The interface morphology of each module wafer was examined using a Hitachi S-4500 field emission gun scanning electron microscope (SEM). Samples for transmission electron microscopy (TEM) were made by simply scratching the wafer surface using sharp forceps. The fine powder resulting was then transferred onto TEM copper specimen grids pre-coated in the usual way for lattice fringe resolution work with perforated carbon thin film. TEM observations were all carried out using a Philips CM-300 machine operated at 300 kV. Chemical composition of the powder contents, including the BN nanorods, was qualitatively checked using an...
FIG. 1. Scanning electron microscopy image showing the following: (a) a large number of nanorods grown on the surface of the silicon wafer. (b) A catalyst particle was often found on one end of a typical nanorod, and the other end of the nanorod shows conical morphology. (c) High magnification SEM image of the catalyst particle shows its faceted surface.

x-ray energy dispersive spectrometer (XEDS), fitted with a super-ultrathin window.

III. RESULTS

A. General

Figure 1(a) is a characteristic low-magnification scanning electron microscope (SEM) image showing that a large number of nanorods cover the silicon surface immediately following the growth phase. The nanorods themselves are usually over 10 μm long and several tens of nanometers in diameter, displaying no preferable nanorod crystallographic axial orientation. It is often found that one end of a nanorod is attached to a prominent bulb, while the other end exhibits a conical geometry [Fig. 1(b)]. The bulbous attachments, which present faceted crystallographic surfaces [Fig. 1(c)], are clearly the bases on which nanorods grow, and have been identified as catalytic particles of an Fe-Si alloy.

A bright-field TEM image of typical nanorods is shown in Fig. 2 in which the cuneiform tips are clearly evident as the final stage of growth [Fig. 2(a)] and catalyst particles are shown in Fig. 2(b). In Fig. 3 we display and underscore major structural features of such a typical nanorod, oriented with respect to its corresponding selected area diffraction pattern (SADP). We note the continuous lattice fringes from one edge of the nanorod to the other, such that the three lattice fringe directions define three corresponding conjoined domains A, B, and C. In each domain the lattice fringes lie parallel to one another, the consistent spacing of 0.34 nm corresponding to {002} planes of hexagonal BN. Well-defined angles are identifiable between adjacent domains. We shall refer to the angle between fringe directions in domains A and C as the apparent apex angle \( \theta_a \). Because of the existence of the intermediate domain B, however, the apparent apex angle \( \theta_a \) thus defined is not identical with those \( \theta_c \) for typical cones where a cuneiform tip is clearly and precisely defined by the sharpness of the fundamental apex itself.\(^{1,11,18}\)

The indexed SADP of the nanorod is shown as Fig. 3(b). The two arrays of diffraction spots (indicated by white arrows) and the faint spots (indicated by black arrows) can be indexed as (00l)'s, due to diffraction from domains A, C, and B, respectively. (100) and (110) direction spot loci are also clearly to be seen in the pattern. The diffraction pattern indicates that the electron beam is more or less perpendicular to the nanorod axis, which means that the angle \( \theta_c \) can be measured from the interangle between the two rows of (00l) spots.\(^{11,18}\) From measurements of some 30 nanorod tips suitably oriented the resulting histogram of the apparent apex angle, a distribution so constructed is displayed in Fig. 3(c). The distribution yields a range of values between 88° to 144°, centered at \( \sim 110° \), and with a standard deviation \( \sigma_{\theta_c} \approx \pm 20° \).

A major feature is the appearance of rows of what appear to be truncated pyramidal voids in the central domain B, indicated by the black arrows in Fig. 3(a) and characterized by the absence of any lattice fringes. These are arranged somewhat periodically along the length of the rod and exhibit the same geometry, while the number of lattice fringes between consecutive voids is close to being identical. Additionally, in domains A and C, dark rectilinear stripes appear parallel to the lattice fringes, as indicated by the white arrows in Fig. 3(a).
The composition of the same nanorod was confirmed by using diagnostic XEDS with a 10 nm electron probe. The XEDS analyses were performed on the three domains separately. The corresponding spectra from domains A and B are shown in Fig. 3d. Only boron and nitrogen signals were, in fact, detected from all three domains and Cu from support grid.

B. Voids

Figure 4(a) is a magnified image of the voids shown in Fig. 3(a). Fringes in adjacent domains define an apparent apex angle of (135° ± 147° − 180°) which is 102°. The two dashed lines in Fig. 4(a) delineate the boundaries between the domains. In the simple schematic drawings shown in Fig. 4(a), the angle between the two dashed lines (domain boundaries) corresponds to an identical interspacing of the lattice fringes, d=0.34 nm, of the three domains. The structure of the BN lattice aggregates surrounding a void imply the presence of a strong interaction between lattice layers in each domain during growth of the nanorod. Attention is also drawn to the clear faceted nature of the void neighborhood in Fig. 4(a) manifested by the darker contrast along the domain boundaries.

C. Dark stripes

The dark stripes in domains A and C clearly have a structural association with the central row of voids overall. Under a proper angle of nanorod tilt relative to the electron beam in the TEM the stripes can often be resolved into what appear to be two-dimensional lattice fringes [see Fig. 4(b)]—resolved atomic columns. The spacing between the spots along the stripe is ~0.22 nm, corresponding to the lattice spacing between {100} planes of hBN indicating that, in this dark stripe, the electron beam is directed down a 100 axis [see schematic diagram for Fig. 4(b)]. While we must keep in mind the well-known turbostratic nature of hBN it is also of note here that the in-basal-plane angular tilt is crystallographic rather than random, and that the black stripes—like the voids—are regularly repetitive, suggesting a mutual association in the wholesale accommodation of structural strain. The possibility that the stripes might be individual stacking faults cannot be ruled out though little experimental information on faults in hBN is available in the literature. We certainly find that experiments to determine the relevant strain vector R in conventional tilt diffraction contrast conditions—such that g ⋅ R = 0 or 1—where g is the operating Bragg diffraction vector, are extremely difficult to carry out on such small nanorods. Clearly, however, the strong
TABLE I. Examples of the dimensions of the nanorods. Three nanorods labeled 1, 2, and 3 are listed with their \( \theta_v \) the apparent apex angle, \( \phi \) the diameter, \( L_{\text{min}} \) the average size of the minimally sized bottom layer, \( L_{\text{max}} \) the average diameter of the maximally sized bottom layers, \( D_v \) the average dimension of the voids along the nanorod axis, and \( D_{se} \) the spacing of the voids along the nanorod axis. \( \theta_v \) is in degree, and the other quantities is in nm. Numbers in parentheses following average quantities represent one standard deviation in the last digit(s).

<table>
<thead>
<tr>
<th>Nanorod</th>
<th>( \theta_v ) (degree)</th>
<th>( \phi ) (nm)</th>
<th>( L_{\text{min}} ) (nm)</th>
<th>( L_{\text{max}} ) (nm)</th>
<th>( D_v ) (nm)</th>
<th>( D_{se} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>99</td>
<td>74.5</td>
<td>3.9(4)</td>
<td>13.5(28)</td>
<td>3.5(10)</td>
<td>12.8(24)</td>
</tr>
<tr>
<td>#2</td>
<td>106</td>
<td>72.6</td>
<td>3.7(7)</td>
<td>9.2(6)</td>
<td>2.1(1)</td>
<td>9.3(7)</td>
</tr>
<tr>
<td>#3</td>
<td>100</td>
<td>44.3</td>
<td>3.6(9)</td>
<td>7.9(12)</td>
<td>2.2(5)</td>
<td>6.4(13)</td>
</tr>
</tbody>
</table>

interlayer interaction demonstrated in Fig. 4(a) also strongly suggests that dark stripes appear to regularly separate zones in domains A and C which display good three-dimensional order. The possibility that the dark stripes might otherwise be twin boundaries cannot be ruled out. It should also be remarked that within the confines of a helical structural model for nanocnical morphology then a superperiodicity of stripes is always a necessary feature. We do not find support for any such strict superperiodicity.

Dimensions of these features of the nanorods are measured from TEM images, and results of three randomly selected nanorods are listed in Table I. The definitions of the quantities listed in Table I are given in the schematic picture of Fig. 4(a). For each nanorod, about 7 nanovoids were measured. Table I also provides data for the diameters, \( \phi \), and the apparent apex angles, \( \theta_v \), of the nanorods, which are typical values measured near the middle of the nanorod; no deviation is quoted since these parameters appear not to vary here. It was found that the spacings of nanovoids, their heights, and the sizes of maximally sized bottom layer of nanovoids show large variations from nanorod to nanorod, while the average size of the minimally sized bottom layer of the nanovoids remains constant at \( \sim 4 \) nm (10 nanorods were measured to check this).

D. Other experimental aspects of structure

The configuration of the \{00l\} atomic layers on the nanorod surfaces is also interesting. In Fig. 4(c) a few BN layers reach out and sheath others presumably deposited before them (see arrows). Conversely [Fig. 4(d)], several closely lying layers connect to form nanoarches which confine an abruptly terminating molecular layer, strongly suggestive of a conventional edge dislocation. Configurations shown in Figs. 4(c) and 4(d) appear to be atomistic methods of enthalpy minimization, where the number of dangling chemical bonds on the nanorod surface are minimized during stages of growth and cooling.

And the detailed structure of the catalyst particles themselves is also important. Figure 5(a) shows a bright-field TEM image of one such particle. The essentially concentric interference fringes indicated by the white arrows are the thickness contours usually observed with thin wedge-shaped crystals, due to \textit{pendellosung} electron Bloch wave periodicities with depth.

The faceted nature of the particle, as seen in Fig. 2(c) is also clearly apparent. Additionally, the particle is usually enclosed by BN layers. Figure 5(b) is a magnified image of the particle showing the interface between the particle and the nanorod, the inset showing an enlarged region displaying lattice fringes, and also the central strip of voids and dark stripes in type C domains. The apparent apex angle here is \( \sim 108^\circ \). To further study the relationship between a catalyst and 045407-4
particle and its associated BN nanorod, individual samples were serially tilted into sequences of orientations and both TEM micrographs and corresponding SADPs recorded. The results clearly demonstrate that catalyst particles have a face-centered-cubic (fcc) structure. In Fig. 5(e), for example, we have a diffraction pattern due to an electron beam incident down a (112) direction in the catalyst particle, the diffraction spots from BN layers being labeled by indices without subscript. A dark field image of Fig. 5(d) was recorded using the diffraction spots of the BN layers indicated by the circle in Fig. 5(c). The orientation of the two close boron nitride (002) diffraction spots coincides here with the \{113\} axis of the particle. The dark field image shows clearly that one-half of the nanorod contributes to the diffraction pattern. It follows that the basal planes of this half of the binanorod are more or less parallel with \{113\} catalyst particle planes. And, in like manner, the second half is parallel to \{200\} axes of the catalyst particle. The apparent apex angle \(\theta_p\) of the nanorod is \(\sim 108^\circ\), which accords with the interangle between \{113\} and \{200\} planes of a catalyst particle with a fundamental fcc structure.

The elemental composition of the catalyst particle was studied by XEDS. Thus, in Fig. 5(e), we find clear boron and nitrogen peaks due to the surrounding BN sheath, while the iron and silicon peaks point to an Fe-Si binary alloy. Structure and composition strongly point to a crystallite of Fe$_3$Si, though we are aware that iron-silicon alloys can be present over a wide stoichiometric range.

Figure 5(f) shows the experimental relationship between catalyst particle diameters and average nanorod widths; the dashed line being drawn simply to guide the eye. Below a particle size of \(\sim 200\) nm, a linear correlation is evident, and the widths of the catalyst particles are approximately 20\% larger than the diameters of the nanorods. However, beyond a particle size of \(\sim 200\) nm, a much smaller slope is observed, the nanorod width being much less affected by the variation of the particle size. In either event, the intimate role played by the catalyst particle in this nanorod growth is perfectly clear.

IV. DISCUSSION

A. Structure

Lattice images [as in Figs. 3(a) and 5(b)] and SADPs [as in Figs. 3(b) and 5(e)] indicate that the nanorod has either a stacked-cone or a helix structure. The presence of voids does, by itself, suggest that a helical model may not apply to the present nanorod, though it is possible that the distribution of the apparent apex angle \(\theta_p\) somehow coincides with that due to a helical structure. This is because the very existence of the voids suggests that more than one nonhexagonal ring could exist in the apical zone (domain B), which would render invalid the discussion of the apex-angle distribution.

The experimental results point to a nanorod structure of stacked faceted cones as schematically illustrated in Fig. 6, the basic internal structural component being a prismatically curved BN basal plane [Fig. 6(a)], which has a bottom facet, \(S_p\), and many side facets represented by \(S_s\)—hereafter simply referred to as layer. It is not unreasonable to suppose that at the conjunction of side and bottom facets nonhexagonal rings may be present, while the interfaces between the side walls are likely to be due to the bending of the BN layer. In order to maintain the intrinsic interlayer spacing for the entire nanorod, since several layers of the \(S_p\) facet are successively deposited, the size of the facet must become progressively smaller [see Fig. 6(b)], and the final locally deposited layer has the smallest local \(S_p\) while along the growth direction, the facets \(S_p\) become larger (refer to the next section of the nanorod growth). Necessarily, however, there must be a minimally sized bottom layer—above a void—beyond which a new layer with a large \(S_p\) forms [see Fig. 4(a) and Table I]. This style of stacking is the fundamental geometrical basis for the periodic appearance of voids along the central nanorod axis [see Fig. 6(b)], and it is implicit that the in-plane crystalline orientation must, in general, be conserved between successive layers. At the atomic bonding level, on the other hand, and allowing for the presence of nonhexagonal rings, we must anticipate that the hexagonal network of hBN will apply commensuration constraints, and that as a consequence relatively large disorientations between layers of a turbostratic nature might appear.

An \(n\)-gonal ring \((n=2, 3, 4, \text{ and } 5)\) can be introduced into a flat hexagonal network by removing an angular wedge or sector of \((6-n) \times 60^\circ\) from the network and by then connecting the two edges together, and the angle then describes the topological defect—a positive disclination—which is responsible for positive Gaussian curvature. In this case, the closed molecular monolayer thus constructed is a nanocone with apex angle \(\theta_{apex}\), geometrically defined by \(n\), i.e., \(\theta_{apex} = 2 \arcsin(n/6)\). In the specific case of BN, any heteroatomic bonding (B-B or N-N) is not strongly favored, thus excluding the need to consider any contribution from triangular and pentagonal rings in the closed BN nanoconical form. It follows that apex angles for a closed monolayer BN nanocone can be only \(19.2^\circ, 38.9^\circ,\) and \(83.6^\circ\), corresponding to a single atom, two atoms, and four-member rings at the cone apex, respectively.

We know that a conical nanorod can also be constructed as a single surface helicoid with an open cone at the apex, the angle of which is determined not only by the apical rings but by a disclination mechanism which favors configurations with high densities of coincidental lattices sites (CLS) be-
between overlapping layers. The apex angles of such open cones are no longer discrete, though specific values are expected due to the disclination’s responsibility for the final topological surface.\(^2\) The distribution of apex angles of nanotubes has therefore been used to distinguish between the two cases—closed and open nanocones—that is nanorods of stacking cones and nanorods of helices. For BN, both cases have been synthesized previously.\(^10,11,18\) A hollow conical helix of BN (BNHCH) has also been studied, which was generated by the simple wrapping of a single beltlike filament similar to a helical structure but without any capping.\(^9,22,23\) Combination of several nonhedral rings can also result in closed conelike structures, as is the case, for example, if nanotube ends are capped, or with interconnecting layers of bamboolike nanotubes.\(^24,25\) In these cases, however, it is not possible to distinguish between stacked conical layers simply by measuring the apex angle distributions.

It is important to note that the BN nanostructures referred to here were synthesized by means of different growth techniques and/or under different growth conditions. The BNHCHs were grown by using CNT substitution followed by a post heating process at an isothermal higher temperature (1750 °C – 1900 °C).\(^9,22\) The BN helical cone particles were produced by heat treating a B-C-N compound to 2200 °C.\(^10,18\) The BN closed cones were part of a material constituted primarily of BN nanotubes synthesized by reacting boron oxide vapor with CNTs under a nitrogen flow at 1500 °C.\(^11\) More recently, a ball-milling and annealing method was documented for growing conical BN nanorods consisting of stacking closed cones, which have a continuous apex angle distribution.\(^16,17\) Different growth mechanisms have been proposed for the formation of these conical structures. Thus, the detailed kinetics for the formation of the BN helical cone particles requires the formation of a broken ring and rapid successive overlap of the BN layers.\(^18\) For BNCH a pre-existing filamentary microstructure, referred to as a microworm, serves as a template. Nucleation of the nanotubes on the microworm surface then leads to a disclination configuration which depends on the curvature of the microworm and the cone size.\(^9\) In both cases the scrolling of the BN layers and thus the axial growth of the BN nanorods are controlled by the disclination mechanism of coincidental lattice sites.

None of these procedures for BN nanorod growth require a part to be played by some catalytic metal particle. In the carbon case, on the other hand, for open conical carbon nanotubes grown on large carbon filaments by using chemical vapor deposition (CVD) method, the shape of the conical filament is assumed to be determined by that of the catalyst particles.\(^26\) Other workers also find catalyst particles to be the disclination source.\(^27\) A catalytic origin might also, of course, be viable for certain other BN conical nanostructures.

**B. Growth**

It is clear that, in the experiments we have described, prior to real BN nanorod growth, there is the necessary precursor stage of catalytic particle formation. This involves decomposition of iron nitrate [Eq. (1)], reduction of iron oxides by Si [Eq. (2)], and homogeneous nucleation of the Fe-Si alloy particles. The stoichiometry of the substrate alloy particles may play an important role in nanorod nucleation but we have not investigated this important aspect experimentally. It is also clear that thermal decomposition of the iron nitrate into iron oxide must be complete after preheating at 500 °C for about 1 hour. On increasing the temperature of the sample up to 1300 °C, we assume that reduction of the iron oxide starts at the interface between the oxide particles and the silicon substrate, and that the initial reduction product is most likely rich in Si. According to the fundamental and well researched Fe-Si binary phase diagram,\(^29\) as the stoichiometry of the iron silicide approaches Fe\(_2\)Si, the particles start melting and their mobility increases. Simultaneously BN is generated \textit{via} the nitriding reaction [Eq. (4)] and BN molecules then diffuse onto the silicon surface from the B\(_2\)C powders. The Fe-Si particles are then the active centers for the heterogeneous nucleation of BN molecules which surface diffuse.\(^28\) We may therefore consider a scenario for growth in which BN basal plane sheets are built up by heteroepitaxy on both the silicon substrate and on the catalyst particle itself. It is not clear whether a firm shielding of the silicon particle by the building up of a single BN monolayer closing the reentrant points where the catalyst particles lie on the substrate is sufficient immediately to cut off diffusing silicon from entry into the catalytic particle, or whether many epitaxial homoepitaxial BN layers accompanied by a small lift-off of the particle is needed. What is certain is that ultimately a sheath of epitaxial crystalline BN covering the particle itself must insulate the particle from any meaningful diffusive entry of Si into the particle. In either event there is a stoichiometric change in a catalyst particle which finally solidifies with an iron component of 75%. This step may be clearly seen in the Fe-Si phase diagram.

During solidification of BN, and growth by homoepitaxy, we must expect a reduction in the number of dangling BN bonds. Simultaneously there is progressive formation of the first BN layers of succeeding cuplike cones. Here the internal volumetric shape typical BN nanorod is one which \textit{mimics} the shape of the tip of the local Fe\(_3\)Si particle but is most certainly not, however, a fully conformal replica [Fig. 7(a)].

The most important process relevant to the growth of BN layers at the intrinsic BN/Fe\(_3\)Si interface is the continuous provision of new BN nuclear layers growing epitaxially on the old. However, if this epitaxial growth were to dominate, the anticipated final product would surely be a tubelike hollow structure or a structure of helical form.\(^18\) Conversely, if the nucleation of new layers dominates then the inevitable result will be a continuous nanorod comprising stained cones only.

Here it is certainly clear that the growth of cuneiform nanorods is manifestly one beginning with the creation of an interface between a classical hBN swiftly epitaxially formed layer due to BN molecular surface diffusion, and the surface of a preformed catalytic particle. It is equally clear that, since the particle remains at the base, then we are observing the consequences of base growth.\(^29–36\) It is important to note that in growth processes of this kind interfaces are relatively fluid in character, while the underlying crystal structure is none
The less firmly enough expressed such that newly arriving BN molecules can be captured and epitaxially built upon so as to establish the ongoing growth of the rod. The physical picture is closely similar to the fluid conditions which are expressed at an interface, or at the surface of a crystal at temperatures slightly less than the melting point. These same conditions are reflected in the macroscopic thermodynamic capillarity of solids, in which minimization of surface energy is the sine qua non for final stability.

Our experimental observations are consistent with the hypothesis that a point is reached when minimizations of both bulk and interface energies are realized at the atomic level by a separation of the basal BN planes from their structured bulk and interface energies; (c) BN building up on top of the catalysis particle completes a void; (d) repetition of processes (b) and (c) results in a nanorod with the central row of voids exhibiting roughly periodic interspacing; (e) the nanorod becomes sharply faceted during cooling and the particle withdraws into a smaller volume.

Once again, then, in simple terms domain B grows, confined by domain growing and separating interfaces A/B and C/B, then defines a growing internal faceting structure upwards from the catalytic particle—the new elemental base being the relatively small BN layer defining the top of the inverted cup of void number 1. However, the growing local elastic field—after the addition of only a few layers—overwhelms the cohesive van de Waals interaction between the BN layers, which eventually pushes the nanorod away from the particle and a second void is generated between the new BN layer and the previous cone [Figs. 7(b) and 7(c)].

The competition is simply one between basal BN layers trying to reach minimum energy internally in simple continuous curvature in the bulk, and the need to crystallize in the given external surface constraints of the nanorod by forming minimal energy surfaces. In the growth dynamics a compromise is reached by the induction of a repetitive process in which zones comprising sharp domains and associated lattice faulting is accompanied by the necessary introduction of a stream of internally faceted voids.

Since the growth is one of relatively steady state, with respect both to the concentration driven feed of BN and the stable growth site temperature, the elastic-induced jump of the catalyst particles is more or less regular, and the central row of voids accordingly exhibits a roughly periodic interspacing [Fig. 7(d)]. In Fig. 8 we show an electron micrograph (lattice imaging TEM) principally displaying a typical projected area of the catalyst particle tip and the base of the BN nanorod after cooling. The implication is that the nanorod becomes sharply faceted during cooling, and that also during cooling into sharper crystalline form the particle withdraws into a smaller total volume so that the first void is now larger than it was during the primary stage of growth [Fig. 7(e)]. The Moiré fringes are due to interference between lat-
In this case the internal structure consisted of a string of true shape transforms of the particle itself, which typically underwent further growth during cooling. Details of nucleation, growth and faceting were also described on the basis of the thermodynamics of the capillarity of solids. Evidently, both base growth and tip growth can take place in the formation of a nanorod during heterogeneous nucleation at a catalytic particle—which is not lifted in the first case, but is in the second. Other experimental factors, including the nature of the moving specie, the strength of its source, the temperature and time, etc., must play a determining role.

It would seem that this theoretical approach might be the basis of understanding for growth and structure of all quasi-one-dimensional structures, from simple SWNT’s onwards, even to solid nanorods, and that a fundamental basis set can therefore be defined.42

V. CONCLUSION

Quasi-one-dimensional BN nanorods comprising prismatic stacked cones incorporating rows of nanovoids—each of which are a partial shape transform of a catalytic particle responsible for heterogeneous nucleation, have been grown by a ball-milling and thermal annealing process. The two key factors responsible are, first, the lift-off and solidification of the catalyst particles and, second, the high nucleation rate of BN clusters upon them due to a dominant surface diffusion. These activities, and the resulting faceted structures, are readily explained by invoking the thermodynamics of the capillarity of solids, including the minimization of the number of surface steps on low index facets at the atomic level, by minimizing the surface energy.

Comminution of particles by ball-milling as a seed supply for controlled nanorod growth remains a remarkably successful prerequisite for nanotube growth. Further control of the growth chemistry means that we now have at our disposal a reliable procedure for the tailoring of quasi-one-dimensional structures in the size, shape, internal and external morphologies we so desire.

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