PERGAMON

Solid State Communications 109 (1999) 555–559

solid state communications

Catalyst effects on formation of boron nitride nano-tubules synthesized by laser ablation

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Received 15 September 1998; accepted 27 September 1998 by Z. Gan

Abstract

The effect of catalysts on the growth of boron nitride nano-tubules (BN-NTs) synthesized using laser ablation was investigated by high resolution electron microscopy (HREM). It was revealed that BN-NTs fabricated with or without catalysts have some differences in atomic layers of the wall, tubule length, surface smoothness, and tip morphology. Based on the experimental evidences, a model is proposed to account for the growth of BN-NTs. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Nanostructures; B. Laser processing; C. Scanning and transmission electron microscopy

1. Introduction

The discovery of carbon nano-tubules (CNTs) [1] has stimulated intensive experimental and theoretical interests in the peculiar rolled-up structures. Based on the similarities between graphitic sheet and hexagonal BN, the existence of boron nitride nano-tubules (BN-NTs) was predicted. Theoretical calculation shows that wrapping of hexagonal BN sheets can produce BN-NTs [2]. On the contrary to CNTs, electronic-structure calculations indicate that the band-gap of the BN-NTs is independent of the diameter and helicity of the tubules [3]. These BN-NTs have semiconductive property with nearly constant band-gap, which provides interesting possibilities for potential applications in electronic nano-devices [4]. It should be noted that most of the BN-NTs were fabricated by arc-discharge method [5–9], while oven-excimer laser ablation technique has recently turned out to be a powerful means for the synthesis of CNTs with single atomic layer and uniform diameter [9,10]. It is well accepted that single-walled nano-tubules are of scientific importance because they make the study of their intrinsic physical properties possible and easy. Recently the BN-NTs were successfully synthesized by the means of oven-excimer laser ablation [11], and it was found that the BN-NTs can be formed with or without adding metallic catalysts. However, the tubules fabricated under these two cases have some differences in thickness of the wall, tubule length, surface smoothness and tip morphology. To our best knowledge, the role of the metal catalysts on the growth of the BN-NTs has not been established. In this letter, we shall report on these differences and propose a model for BN-NTs growth, which may be useful in understanding the role of catalyst in the growth of BN-NTs and optimizing the catalytic

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0038-1098/99/$ - see front matter
PII: S0038-1098(98)00541-9

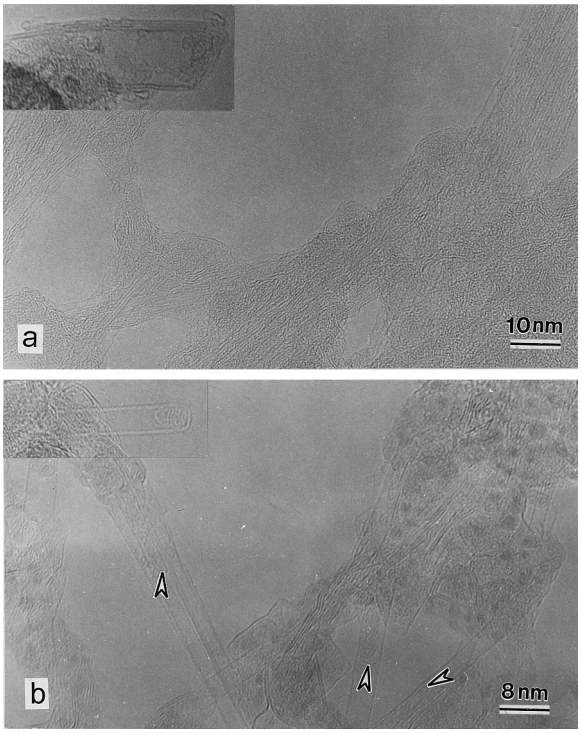

Fig. 1. Typical HREM micrographs showing general morphologies of the BN-NTs synthesized by laser ablation. The arrow heads indicate amorphous BN clusters. The inset shows the typical tip morphology. (a) The BN-NTs synthesized without the catalysts. The number of atomic layers are more than 2 in wall thickness and the tubule surface is rough. (b) The catalytically grown BN-NTs. They are mainly single atomic layer-walled tubules and the surface is clean.

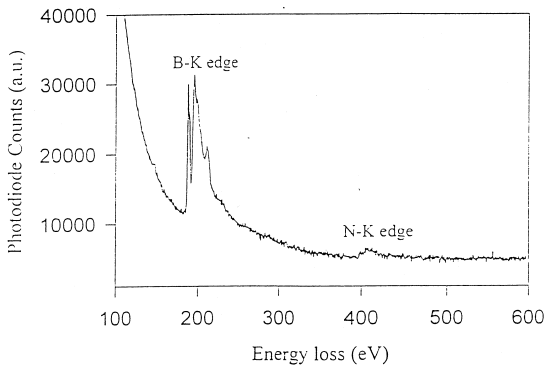

Fig. 2. PEELs spectrum taken from an individual BN-NTs. The distinct absorption peaks at 188 and 401 eV correspond to the B–k edge and N–k edge, respectively.

process for producing single atomic layer wall of BN-NTs.

2. Experiment

The BN-NTs were synthesized by the same oven-laser ablation method used for synthesizing single-walled CNTs [10]. The target materials were prepared by hot-pressing pure BN powder with or without nano-sized Ni and Co powder catalysts. The target was placed inside a quartz tube heated by a furnace. The quartz tube was first evacuated to a vacuum about 20 mT, then filled with flowing Ar carrier gas. An excimer laser was used as the evaporating source to ablate the target at 1200°C. The ablated species carried by the flowing carrier gas were collected by a water-cooled collector mounted downstream inside the quartz tube. The product was dispersed in ethanol and deposited onto carbon grids for characterization by transmission electron microscopy. HREM study was carried out in a JEM-2010 microscope operated under 200 kV with a point resolution of 0.194 nm. The parallel electron energy loss spectrum (PEELs) was performed in a Philips CM-200FEG microscope equipped with Gatan Image Filter (GIF).

3. Results and discussion

Tubular structures of boron nitride can be synthesized by laser ablation with or without Co–Ni catalysts. Fig. 1(a) shows the product synthesized without catalyst and Fig. 1(b) shows the catalytically grown product. From Fig. 1(a), it can be seen that the tubules wall is more than two atomic layers in thickness and the tubules diameter ranges from 1.5 to 6 nm. The outer surface of the tubules is rather rough. The inset in Fig. 1(a) is a magnified HREM image of BN-NTs synthesized without catalysts. It is visible that its tip morphology is irregular-shaped and some attachments are observed on the outer surface of the tubule. From Fig. 1(b), it is found that the catalytically grown BN-NTs are mainly single-walled and their diameter ranges from 1.5 to 4.5 nm. The outer surface of tubules is clean without any attachment. The inset shows the tip morphology of BN-NTs synthesized with catalysts. According to our observations, the length of catalytically grown BN-NTs is longer than

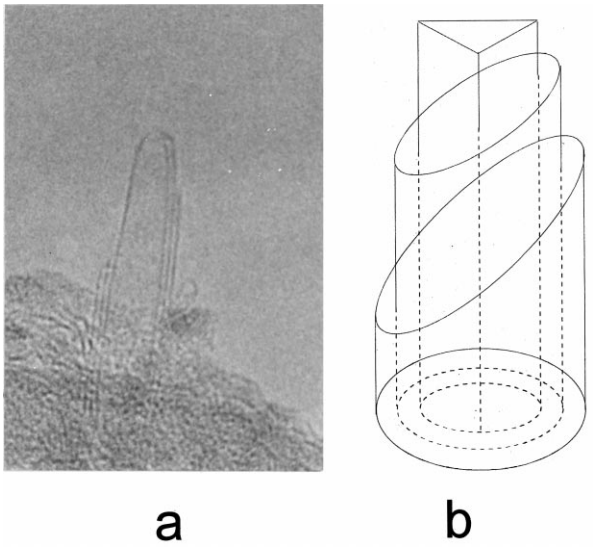

Fig. 3. Open-end growth model for the BN-NTs. (a) A BN-NT tip morphology. The outer atomic layers are not enclosed. (b) Hodograph of the growth velocities of BN-NTs. The growth velocity of the inner atomic layer is faster than that of the outer layer. The growth velocity is also different on an atomic layer. The locus of active sites for a growing atomic layer is an ellipse.

that of the BN-NTs synthesized without catalyst. It is interesting to note that all the nano-tubules have amorphous inclusions at the middle or tip, as is indicated by the arrows in Fig. 1, which may be related to the growth process of the tubules.

The bonding state and chemical composition of the nano-tubules were determined by PEELs as shown in Fig. 2. The spot size of the electron probe is about 2 nm in diameter. The spectrum taken from a single nano-tubule shows clearly the presence of boron and nitrogen, and the absence of carbon. Quantitative analysis of the PEELs gives the B : N ratio of 1 : 0.8. This value, with consideration of the error about 20% owing to background subtraction, is close to the stoichiometric B : N ratio in hexagonal BN. In addition, the chemical composition of amorphous inclusions in the BN-NTs were also determined as being only B and N by PEELs analysis.

Carefully examining the tip morphologies as shown in the insets of Fig. 1, we found that no metallic particles were visible inside the tubule, which were supposed to play a role on the growth kinetics of BN-NTs [4]. These peculiar tip morphologies of BN-NTs are also different from the conical caps of CNTs. The conical tips can be formed only by introducing pentagons into the hexagonal network. In the BN system, however, introduction of pentagon into the graphitic type network will unavoidably cause B–B and N–N bonding, which is energetically unfavorable. In order to avoid this type of energy frustration, a closure by a triangular facet, resulting from three 120° disclinations is proposed [5].

Fig. 3 shows another BN-NT tip morphology synthesized with catalysts. It is interesting to note the most inner wall of the tip is completely closed, however, the second and third atomic layers are partially grown. In the growth process of carbon nano-tubules (CNTs), the open-end growth model of the nano-tubules and template growth model for multi-layer were presented [12]. However, there is no report on direct experimental evidence to justify this proposed mechanism. Fig. 3 provided some experimental clues for the open-end and template growth model in the growth process of BN-NTs. According to our observation, most of the tubules are attached to amorphous BN cluster at one end and the other end is free. As long as the tubule end is open, B, N atoms can be deposited onto the tubule peripheries, and the tubule grows continually. The outer layer can nucleate and grow because of the template of the inner layer. So the multi-walled nano-tubules result from the layer by layer growth

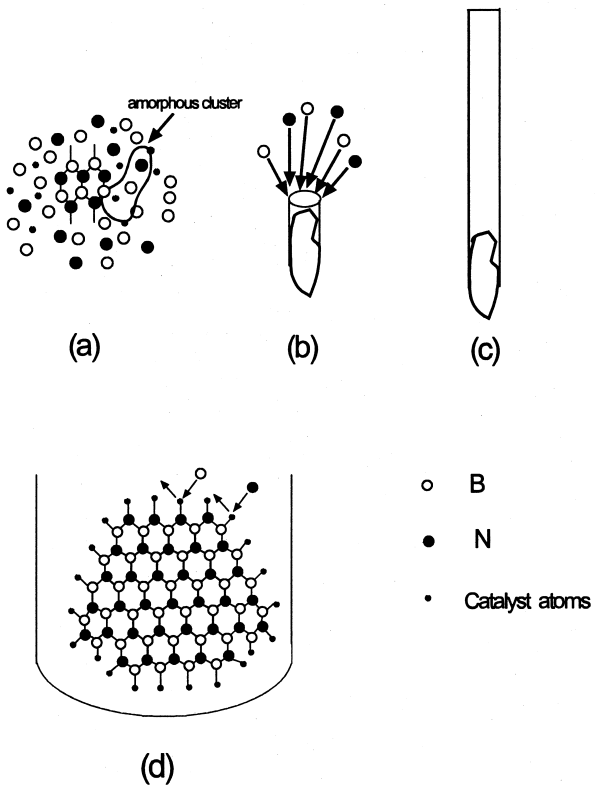

Fig. 4. Schematic presentation of proposed growth model of the BN-NTs: (a) Laser ablation creates cloud of single B, N atoms, h-precursors, catalysts atoms and amorphous clusters. (b) The B, N atoms and h-precursors stick onto the amorphous clusters as the nucleation sites of BN-NTs. The B, N atoms chemisorb on the dangle bands of h-precursor which is the growth embryo of the BN-NTs. (c) The nano-tubules are closed by introducing the flat cap. The second atomic layer may nucleate and grow because of the template of the first layer. (d) Schematic representation of the effect of catalysts atoms on the BN-NTs growth. The dangle bonds are first stabilized by the catalysts atoms. The supply of B and N atoms kicks out the catalysts atoms and occupy these positions because they can develop into more stabilized band structure with the dangle bands.

on tubule side-wall involving thickening of the tubule. From Fig. 3(a), it is found that the growth velocity of the inner layer is faster than that of the outer layer, which may be related to the catalyst effects which makes the axial growth faster than that of the radial growth. The growth velocity is also different on an atomic layer. The locus of active sites for a growing atomic layer is an ellipse, just as shown in Fig. 3(b). The difference of growth velocity on an atomic layer results from the heterogeneous deposition of B and N atoms along the periphery of open-end atomic layer. In contrast, it can also be inferred that the dangling bonds of B and N atoms at the peripheries of the open tubule ends can be stabilized by catalyst atoms, otherwise, this kind of open-end structure will be unstable and the end of tubule will adopt closed configuration. This is different from the CNTs, in which the open-end structures are rarely found.

During the laser ablation process, Ar gas flowed downstream the quartz tube, carrying the formed BN-NTs down towards the rear of quartz tube and the nano-tubule materials were collected at the water-cool collector. According to the earlier mentioned facts, a plausible growth mechanism is proposed to explain the formation and structural characteristics of BN-NTs, as is shown schematically in Fig. 4. The key factors in the growth of BN-NTs are nucleation and driving force of further growth. Under the laser ablation, the target is decomposed into single B, N atoms, h–BN precursors, catalysts atoms, and

amorphous BN clusters (Fig. 4(a)). The cloud of these ablated species flows downstream the quartz tube with flowing Ar carrier gas. As the velocity of thermal motion of the atoms and precursors is faster than that of the amorphous clusters, B, N atoms and h–BN precursors in the cloud can stick onto the amorphous clusters which are the nucleation sites of the BN-NTs. B, N atoms chemisorb on the dangle bands of h-precursor which is the growth embryo of BN-NTs (Fig. 4(b)). The second factor is driving force for the further growth of BN-NTs. There are two models postulated to explain the open-ended nano-tubules growth, in which the driving force for further growth of nano-tubules is temperature gradient or electric field [13,14]. According to our experimental conditions, we think that the further growth of BN-NTs is mainly caused by thermal gradient during the growth process of the BN-NTs. Theoretical calculation shows that thermal gradient at the nano-tubule tip can give rise to non-equilibrium force that could favor the open geometry of the nano-tubule tip. According to Monte Carlo simulation, there also exists the lowest tubule tip temperature necessary for the growth of nano-tubules [14]. The nano-tubule will be enclosed by introducing the flat cap when it moves to a critical temperature zone where the temperature is lower than the minimum temperature needed for nano-tubule growth, so the tubule tip becomes inactive and there is no more further growth on that particular tubule shell.

In catalytic growth of CNTs, metal catalyst particles were frequently observed encapsulated inside the nano-tubule, either in the middle or at the tip part of nano tubules. It is therefore speculated that the catalyst particles act as a transporter, and as a nucleation site where the CNTs can grow. As opposed to the CNTs formation on transition metals, the nano-sized catalyst particles are not encapsulated inside the BN-NTs. Meanwhile the BN-NTs can also be synthesized without catalyst. This reveals a difference compared to the previous postulation in the growth of CNTs. Theoretical calculation [9,10,14,15] shows that the dangling bonds can be stabilized by the metallic atoms, and act as attractive sites for the deposition of B and N atoms (Fig. 4(d)). So of axial growth rate BN-NTs is much higher than the radial growth because of the catalysts effect. As a result, the catalytically grown BN-NTs have longer length and fewer atomic layers than that of the BN-NTs synthesized without catalyst. In contrast, the B and N atoms can catalytically chemisorb on the strict hexagonal network of growing sites owing to the catalyst effects. If there are no catalytic atoms to stabilize the dangling bonds, the forthcoming atoms may irregularly chemisorb on the growing sites. This will give rise to the roughness of the tubule surface.

4. Conclusion

BN-NTs were successfully fabricated by laser ablation with or without the catalysts. It seems that the open-end growth model is mainly responsible for the growth of BN-NTs. The catalysts may play an important role in the growth of tubule by keeping the dangling band and opening the graphitic network.

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