

Growth of Boron-Rich Nanowires by Chemical Vapor Deposition (CVD)

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B-rich nanowires are grown on Ni coated oxidized Si(111) substrate using diborane as the gas precursor in a CVD process at 20 torr and 900°C. These nanowires have diameters around 20–100 nanometers and lengths up to microns. Icosahedron B₁₂ is shown to be the basic building unit forming the amorphous B-rich nanowires as characterized by EDAX, XRD, XPS, and Raman spectroscopies. The gas chemistry at low [B₂H₆]/[N₂] ratio is monitored by the in situ mass spectroscopy, which identified N₂ as an inert carrier gas leading to formation of the B-rich compounds. A nucleation controlled growth mechanism is proposed to explain the rugged nanowire growth of boron. The role of the Ni catalyst in the synthesis of the B-rich nanostructures is also discussed.

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1. INTRODUCTION

Motivated by the extensive research on carbon nanotubes (CNTs), boron and its related nanostructures have also attracted increasing interests for their potential applications in nanodevices and nanotechnologies due to their extraordinary properties. Boron has a high melting point ($\sim 2300^\circ\text{C}$), low density ($d = 2.35\text{ g/cm}^{-3}$), good resistance to corrosion, and it is also one of the harder materials ($H_v = 3000\text{ kg}$) [2]. Moreover, boron and boron-rich compounds are semiconductors with unique electronic properties controlled by the icosahedron structures. Recently nanoclusters of quasicrystalline boron, in the forms of convex, spherical, quasi planar, and tubular geometries, have been calculated from ab initio study in which the basic unit cells of these quasicrystalline boron nanoclusters are composed of two different rhombohedra cells containing B₁₂ icosahedron [1]. These boron nanotubular clusters are predicted to be metallic conductors independent of the structural chirality with stronger covalent intertubular bonds compared to CNTs via van der Waals bonding. Due to these potential properties, boron is a good candidate for use in high-temperature devices, fusion reactor wall components, thermoelectric energy conversion, and elemental semiconductors [2].

Recently, some experimental research work has been done on boron nanostructures. Single-wall boron nanotubes (BNTs) were reported by Ciuparu et al. [3], however, they showed high sensitivity to electron beam leading to difficulty in the detailed characterization of the tubular structures. Several groups synthesized amorphous or crystalline boron nanowires (BNWs) by RF magnetron sputtering [4], laser ablation [5–7], and chemical vapor deposition [8]. BNW growth by the vapor-liquid-solid (VLS) mechanism had been proposed [5], but no tip attachment of the catalyst particles was found at the end. In addition, this mechanism cannot be applied to BNWs formed without any catalyst on various substrates [4, 8]. Another suggestion of vapor-solid (VS) growth mechanism [6, 7] was advanced in which the solidification of boron or boron oxide vapor could be the key to explain the BNW growth. But, it is still not clear in this model that the factors, such as supersaturation level of B precursors in vapor phase, the complex structure of boron clusters, could play a role in the anisotropic growth of boron wires.

In this study, a simple and effective way of fabricating boron nanowires (BNWs) using a cold-wall CVD process is proposed. The effects of gas composition, temperature, and pressure are investigated. The role of the catalyst in the synthesis is also demonstrated.

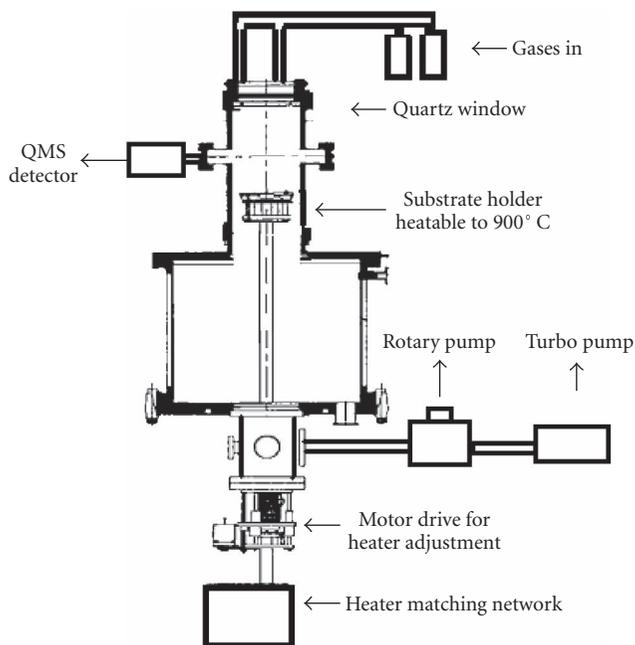


FIGURE 1: Schematic of the CVD system.

2. EXPERIMENTAL

Boron-rich nanowires were synthesized in a cold-wall CVD system as shown in Figure 1. The process employed diborane (B_2H_6 , 5 vol% diluted in H_2) as the gas precursor for B and nitrogen (N_2) as the carrier gas. A 20 nm-thick Ni thin film was deposited on oxidized Si(111) substrate by electron beam evaporation. After the CVD system was evacuated to 10^{-6} torr and $350^\circ C$, the substrate was heated to $900^\circ C$ for 10 minutes in N_2 gas flow for creating catalyst islands. Diborane gas was then introduced for deposition for 2 hours at 20 torr and $900^\circ C$. The total flow rate of gases was 60 sccm, in which diborane was 5 sccm and nitrogen was 55 sccm.

In situ mass spectroscopy (MKS Instruments Orion Compact) of the gaseous phase was used to identify the chemical reactants and products during CVD process, which provided additional insight on the growth species during deposition. Temperature of the substrate surface was monitored by an infrared pyrometer (Raytek Thermalert GP). After depositing for 2 hours, grey products collected from the substrate were analyzed by ESEM (environmental scanning electron microscope) and TEM (transmission electron microscope), and further characterized by Raman spectroscopy (Micro-Raman T64000 Jobin Yvon triple monochromator system), XPS (X-ray photoelectron spectroscopy), and EDAX (energy dispersive analysis by X-ray).

3. RESULTS AND DISCUSSION

Uniform nanowires were synthesized on Ni coated oxidized silicon(111) substrates. Figure 2 shows the typical ESEM images of the nanostructures with diameters around 20–100 nanometers and lengths in microns. Most of Ni catalyst islands formed due to surface tension during heating process

were much larger in comparison to the boron nanostructures. TEM analyses (see Figure 3) revealed the presence of two different types of growth; (i) uniform and bamboo-like nanowires without the catalyst attachment, and (ii) straight nanowires with Ni particles encapsulated at the tip. When catalyst particles are involved in the growth, their sizes determine the diameter of the nanostructures. Small Ni particles (not more than 100 nm in this case) are attached to the tip of the nanowires. Due to the thick Ni film (20 nm in this case), most of the Ni islands are of diameter around 200 nm. The weight of the big catalyst islands prevents them from rising up during growth. These nanostructures were characterized by electron diffraction, which revealed an amorphous nature of the B-rich phase. These results are also consistent with the X-ray diffraction data shown in Figure 4 in which the only sharp peak is from the Si substrate.

The composition of the deposited nanostructures was determined by EDAX analysis shown in Figure 5. The main constituents in the surface deposits are B, Ni, O, and Si, in which Ni is from the catalyst thin film and Si and O are mainly from the oxidized Si substrate. The percentage of B is about 94.53 at %, and no appreciable amount of N (0.19 at %) is detected. The corresponding XPS spectra indicate the presence of B-rich structures from both elemental and atomic chemical states of the products. Figure 6 shows the binding energies of B 1s, N 1s, and O 1s. One of the deconvoluted B 1s peaks at 189.0 eV corresponds to the B–B bond, and the peak at 193.1 eV indicates a small amount of the B–O bond. The N 1s signal shows a main peak at 400.2 eV, which could be attributed to the contamination from N–O bond. Since only one O 1s peak at 533.2 eV was detected in the sample, probably the small amount of O along with N forms the compound B–O–N in the deposits [9]. Thus, the nanofeatures appear to be boron-rich materials.

Figure 7 shows the deconvoluted Raman spectra of the boron-rich nanowires. Peaks centered at 1070 cm^{-1} have been associated with the vibration mode of intericosahedral B-B bonds (length of 1.70 \AA), in which neighboring B atoms of adjacent icosahedra vibrate against each other [10]. The peaks located from 600 cm^{-1} to 900 cm^{-1} (702.7 cm^{-1} , 809.8 cm^{-1}) represent intraicosahedral vibration modes, which arise from vibrating of B atoms in an icosahedra unit (bond length of 1.76 \AA), having A_{1g} or E_g symmetries [10, 11]. The spectrum also shows features in the range of 300 cm^{-1} to 600 cm^{-1} (centered at 534.0 cm^{-1}), which could be assigned to stretching modes of boron bonded to foreign atoms (N or O in this case), which are minor in the deposits [11, 12]. The fourth peak centered at 243.5 cm^{-1} could be attributed to the chain structures connecting B_{12} icosahedra [11, 12]. The presence of B_{12} icosahedra shown by Raman spectrum supports the theoretical prediction of basic unit cells to form the boron nanoclusters. The broadened Raman peaks also support the noncrystalline characteristic (quasicrystalline or amorphous) of these clusters, which is consistent with the electron diffraction and XRD data.

Before discussing the growth mechanism of the B-rich nanowire structures, it is pertinent to examine the chemistry

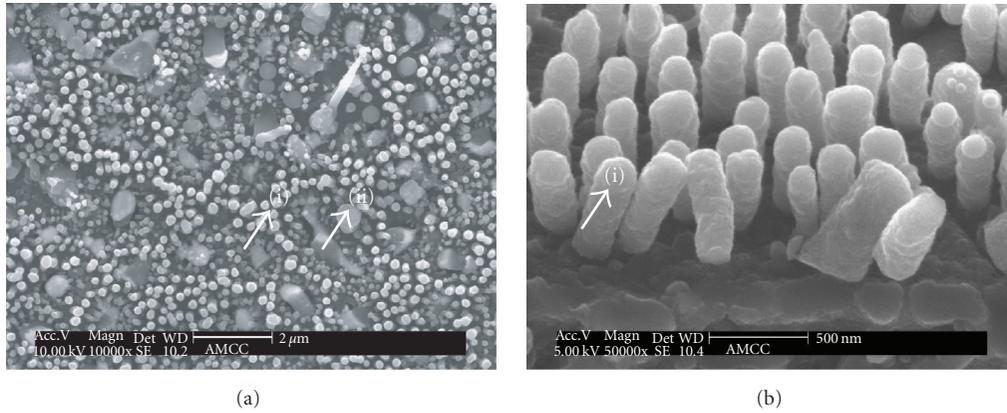


FIGURE 2: ESEM images of BNWs on the Ni coated oxidized Si(111). The big Ni particles (ii) are surrounded by BNWs (i) of small diameters. (a) Top view. (b) Edge view when the substrate was tilted by 45°.

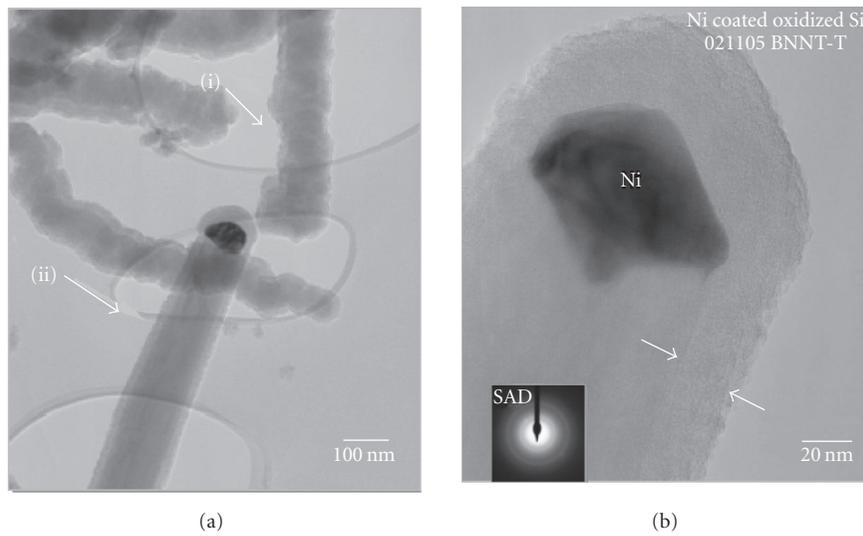
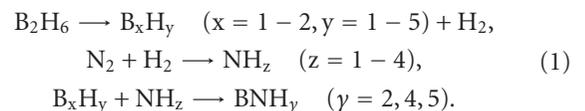


FIGURE 3: TEM images of the Ni coated oxidized Si substrate revealing the presence of two distinctly different types of boron-rich nanowires; (i) uniform and bamboo-like and (ii) smooth and Ni capsulated surface. The dark regions correspond to metallic Ni particles. The arrows in (b) indicate the 15 nm outer shell of the Ni involved nanowires. Note that all nanostructures analyzed appeared amorphous (see corresponding electron diffraction pattern inset in (b)).

of the reactant gases during deposition. In situ mass spectroscopy of the gaseous phase is used to identify the chemical reactants and products, which provided information on the reaction pathways during CVD. Figure 8 shows active species detected in the gas phase at substrate temperature of 900°C. Diborane (B_2H_6) is a common group III gas reactant, which completely decomposes above 300°C and diffuses into bulk materials quickly [13]. Therefore, only a small amount of the decomposed B_xH_y species is detected in the gas phase (such as BH_2 , BH_3). In our case, N_2 was used as the carrier gas, which partially dissociated during deposition. However, due to its inertness compared to ammonia, the ratio of active-nitrogen species to diborane is expected to be much less than the calculated values based on the complete dissociation of

N_2 , which could be one of the reasons for small amount of B–N bonds that are found in the deposits. The reactions occurring in the gas phase can be described in three steps; (1) decomposition of diborane, (2) combination of nitrogen and hydrogen, and (3) reaction of B_xH_y and NH_z , by the following equations [14]:



The low concentration of the intermediate compounds (BNH_y) in the gas environment may be one of the reasons for little incorporation of N into BNWs synthesis in this study.

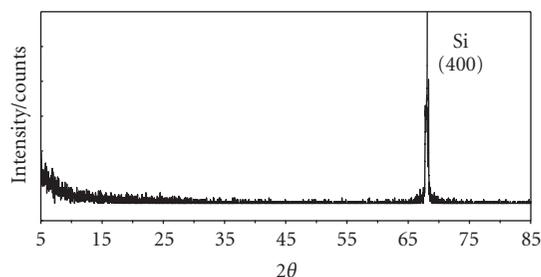
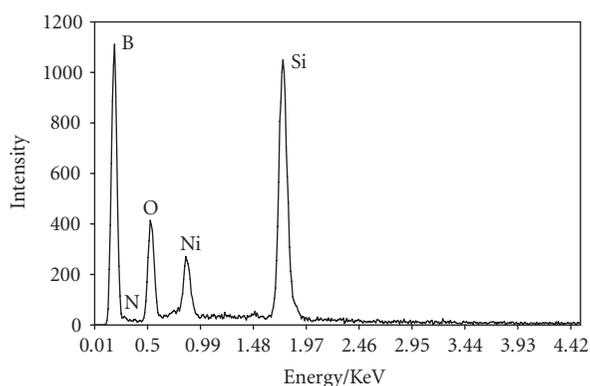


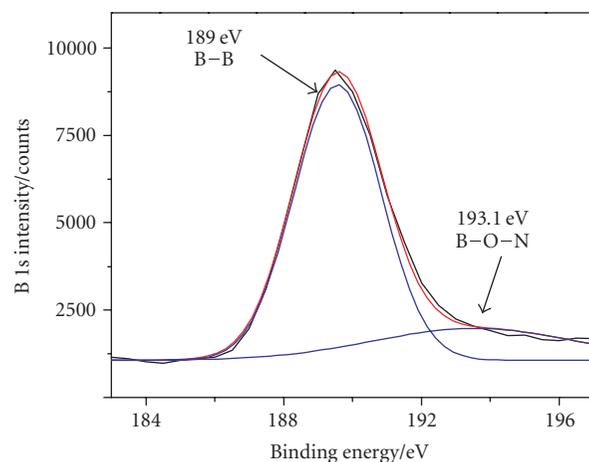
FIGURE 4: XRD pattern of B-rich nanostructures on Ni coated oxidized Si substrate.



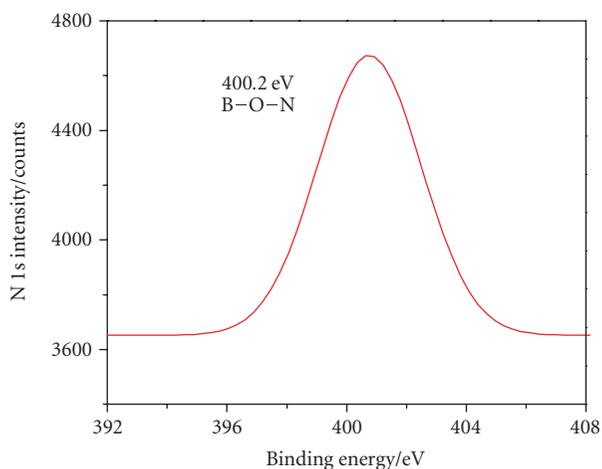
Element	Wt %	At %
B K	87.9	94.53
N K	0.23	0.19
O K	2.99	2.17
Ni L	2.65	0.53
Si K	6.23	2.58

FIGURE 5: EDAX spectrum of the Boron-rich nanowires.

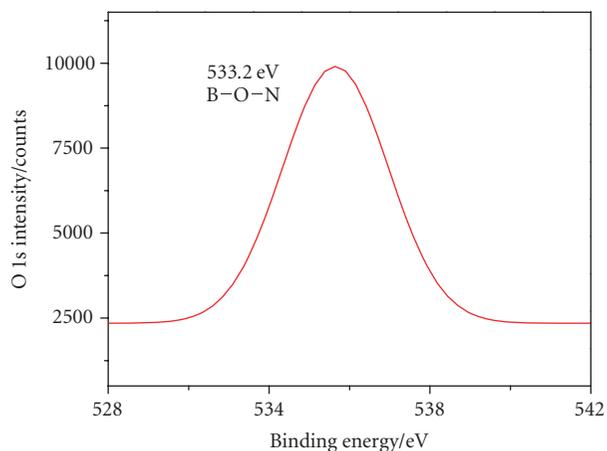
A surface nucleation controlled growth mechanism is proposed for boron-rich nanowire. First, decomposition of the diborane gas happens when it gets close to the heated substrate, which releases the boron source from the gas phase. Then, nucleation of the small B particles takes place on the surface, which forms active precipitation sites (see Figure 9(a)). The significant level of decomposed B from the feed gas migrates randomly on the surface towards the active sites and starts to accumulate on them. This accumulation happens in two ways (see Figure 9(b)). The growth of nanowires is mainly through precipitation of B from the vapor phase, and secondary nucleation can also take place on the surface of grown nanowires (see Figure 9(c)). Thus, a three-dimensional growth model is set up, in which two processes take place at the same time; (i) surface nucleation and growth of decomposed B from the gas phase on the top of nanowires, and (ii) accumulation of B around grown precipitate. The consecutive surface nucleation leads to the formation of rugged surface of nanowires (see Figure 9(d)). Figure 9(e) shows the ESEM image of rugged as-grown nanowires with small nucleation on the top, which is consistent with the proposed mechanism.



(a)



(b)



(c)

FIGURE 6: (a) B 1s, (b) N 1s, and (c) O 1s XPS profiles of the boron-rich nanowires.

Catalyst is not necessary for the growth of B-rich nanowires of this study because boron nucleation does not have any preferential sites. However, when catalyst particles are

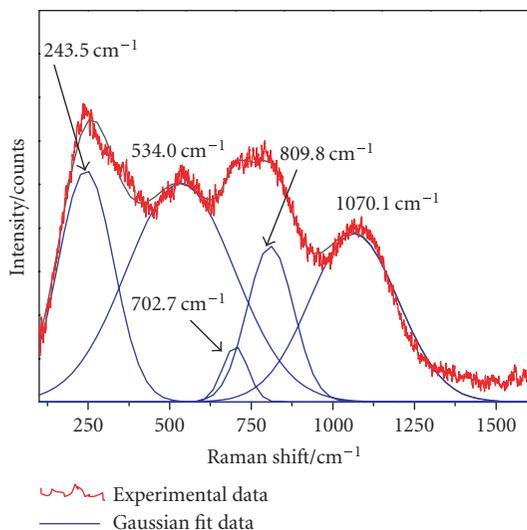


FIGURE 7: Raman spectra of boron-rich nanowires on Ni-coated oxidized Si substrate.

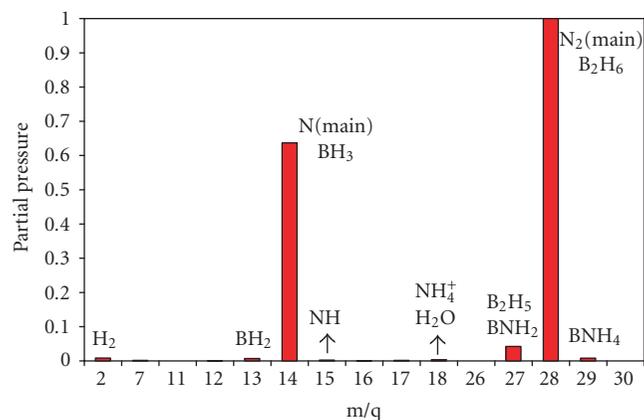


FIGURE 8: Active species detected during CVD of boron-rich nanowires at a $[B_2H_6]/[N_2]$ ratio of 0.0045 using quadrupole mass spectroscopy (QMS). The partial pressures of all species are normalized by partial pressure of N_2 .

involved in the growth, the VLS growth mechanism [15] may be applicable to the boron-rich nanowire growth. Small Ni nuclei form due to surface tension upon heating the substrate with very thin Ni film. Subsequently, when diborane gas is introduced into the reaction chamber, the decomposed boron might react with the nickel catalyst to form the nickel borides (Ni_2B , Ni_3B) on the surface of Ni islands which could decrease the melting point of Ni dramatically from $1400^\circ C$ to $\sim 1000\text{--}1100^\circ C$ [13, 16]. On the other hand, the size effect of nanoscale structures can result in further decrease of the melting points, compared with the bulk materials [15]. Both of these facts help to produce liquid phase on the Ni islands. The continuous supply of B from the gas phase gets into the Ni islands and reacts with the Ni particles, leaving a coexisting system of Ni and NiB_x . When dissolved B reaches

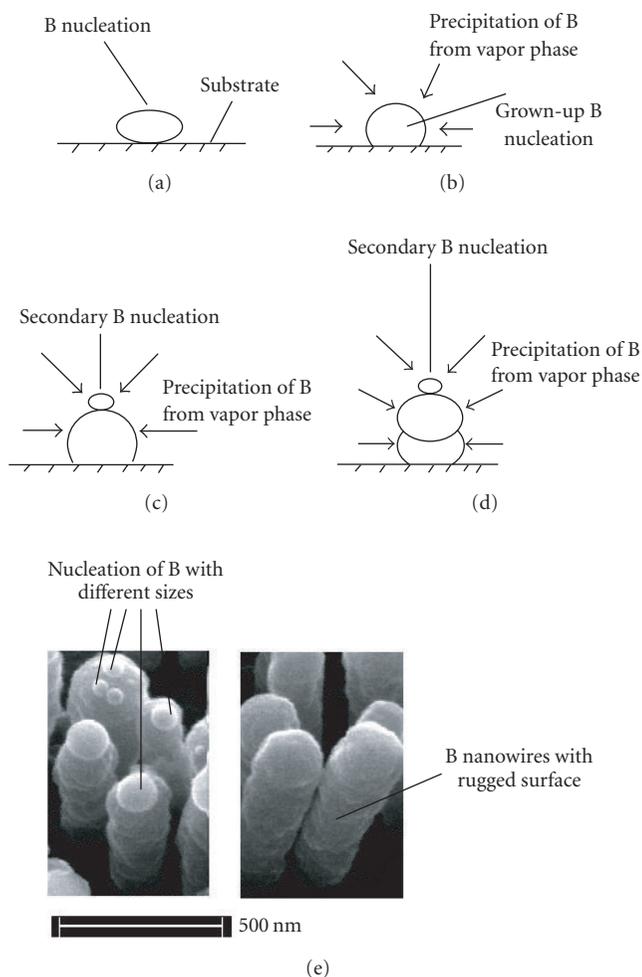


FIGURE 9: Schematic process of the proposed nucleation controlled growth mechanism for boron-rich nanowires.

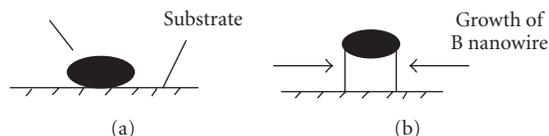


FIGURE 10: Schematic process of the proposed growth mechanism for Ni-catalyzed boron-rich nanowires.

its saturated status, it will precipitate out and accumulates on the Ni particles. Since Ni particles cannot grow during the nanowires growth, there is no chance for the secondary nucleation to happen, which helps to eliminate the bamboo knots and leads to BNWs of uniform radius as shown in Figure 10.

4. CONCLUSIONS

Amorphous B-rich nanowires with diameter around tens of nanometers and lengths up to microns were grown on

Ni coated oxidized Si(111) substrate using diborane as the gas precursor in a CVD process at 20 torr and 900°C. The presence of B₁₂ icosahedron inferred from Raman spectrum provided the theoretical prediction of B₁₂ containing basic unit cells to form the quasicrystalline boron nanoclusters. TEM analysis revealed the presence of two different types of growth; (i) uniform and rugged nanowires without catalyst attachment and (ii) straight nanowires with Ni particles encapsulated on the tip. A consecutive nucleation involved growth mechanism was proposed to explain the rugged wire growth. Ni catalyst was not necessary for the synthesis of the B-rich features. However, VLS growth mechanism was suggested for the straighter and size-dependent wire growth when the Ni catalyst was involved.

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