One-dimensional boron nanostructures: Prediction, synthesis, characterizations, and applications

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One-dimensional (1D) boron nanostructures are very potential for nanoscale electronic devices since their physical properties including electric transport and field emission have been found very promising as compared to other well-developed 1D nanomaterials. In this article, we review the current progress that has been made on 1D boron nanostructures in terms of theoretical prediction, synthetic techniques, characterizations and potential applications. To date, the synthesis of 1D boron nanostructures has been well-developed. The popular structures include nanowires, nanobelts, and nanocones. Some of these 1D nanostructures exhibited improved electric transport properties over bulk boron materials as well as promising field emission properties. By current experimental findings, 1D boron nanostructures are promising to be one of core materials for future nanodevices. More efforts are expected to be made in future on the controlled growth of 1D boron nanostructures and tailoring their physical properties.

1. Introduction

The rapid development of nanoscience and nanotechnology has inspired the community with great interest to explore new features of existing materials as well as novel materials at nanoscale. Nanomaterials, in general, refer to materials with their size, or at least one dimension, down to the range of 1–100 nm.¹ Their popular forms include zero-dimensional (0D) and one-dimensional (1D) nanostructures. 0D nanostructures

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are well-known due to the significant progress, for instance, on quantum dots,² with which as model systems many fundamental concepts have been learned by manipulating their sizes and shapes.³ By employing these quantum dots as building components, various novel applications have been developed, including memory media,⁴ quantum lasers,⁵ optical sensors,⁶ and single electron transistors.⁷ Since the discovery of carbon nanotubes, 1D nanostructures have also been intensively studied as one focus of nanomaterials research because of their unique shape and properties for building nanodevices. It is well recognized that 1D nanostructures offer an ideal model to study the dependence of electron transport, thermal conductivity, and mechanical strength on dimensionality and size reduction.¹ The quantum confinement effect arising from their small size enables 1D



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nanostructures to show novel electron transport properties that aren't exhibited in the bulk.^{8–11} Their high surface-to-volume ratio makes 1D nanostructures very appealing for catalytic reactions as photocatalysts or support materials.^{12,13} Their size confinement in one dimension also renders a high optical gain, faster operation speed, and tunable band gap to afford applications in optoelectronic devices and optical sensors.^{14,15} Much of literature has been published in the past two decades regarding synthetic methods and applications of 1D nanostructures with various materials, such as metal oxides (ZnO, In₂O₃, SnO₂) nanowires,^{16–19} group IV (C, Si, Ge) nanotubes/nanowires,^{20–24} group III–V (InAs, AlN, BN) nanotubes/nanowires,^{25–27} group II–VI (CdSe and ZnSe) nanowires^{28–30} *etc.* Using these 1D nanostructures, various nanoelectronic devices have been developed, including field-effect transistors,^{31–33} direct-current nanogenerators,³⁴ light-emitting diodes (LEDs),^{35–37} thermoelectrics,^{38–40} complex logic gates,⁴¹ field emission displays,^{42–45} and sensors.^{46–48}

This article reviews the current progress on one-dimensional boron nanostructures in terms of prediction, synthesis, characterization, and potential applications. Boron is a p-type semiconductor with a band gap of ~ 1.56 eV. It is the only non-metal element in group III and shows some similar properties to its neighbor carbon and diagonal relative silicon. Although boron is an electron deficient atom and the number of valence electrons is lower than that of available orbitals, its small size and high ionizing energy favor covalent bonding rather than metallic bonding. It makes boron form the B₁₂ icosahedra structural unit through a unique 3-center 2-electron bond, based on which, boron has unique physical and chemical properties such as low



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transportation properties and field emission properties of onedimensional nanomaterials with low work function, investigation of their formation mechanism and applying them to nanoscale devices.



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frontier of nano-electronic materials and device physics using scanning probe microscopy/spectroscopy for self-assembly mechanisms at interfaces and physical properties of single molecule quantum structures. density, high melting point, extreme hardness, and high chemical stability.⁴⁹⁻⁵¹ It has been widely used as a dopant in the semiconductor industry and its compounds play essential roles in light-weight structural materials.⁵²⁻⁵⁴ Inspired by the first theoretical work on boron nanotubes⁵⁵ and the prediction of high electrical conductivity of 1D boron nanostructures, ⁵⁶⁻⁵⁸ the developments in 1D boron nanostructures including nanotubes, nanowires, nanobelts, and nanocones have attracted great attention from both science and engineering communities in recent years. These 1D boron nanostructures are expected to serve as core components for the next generation of nano-devices, such as high-temperature semiconductor devices, field effect transistors, field emission devices, as well as superconductors.

2. Theoretical prediction of boron nanostructures

Following Moore's law, the size of transistors has reached the nanoscale and conventional silicon based CMOS devices will meet possible physical challenges in nanoelectronics. In the past decades, although single carbon nanotubes (SCNTs) are regarded as promising candidates for these applications, chirality dependent electronic properties make this more problematic. Therefore, searching for promising new nanotubular materials with unique properties is highly desirable. Small boron clusters with novel properties would be a topic worth reviewing. In 1996, Boustani et al. first reported that a nanotubular boron structure can consist of B₂₄ clusters using *ab initio* quantum-chemical and density functional methods.55 In order to understand the formation mechanism of boron nanotubes, the electronic and geometric structures calculations were performed on small boron clusters B_n (n = 2-14), based on *ab initio* quantum-chemical methods and a restricted Hartree-Fock self-consistent-field approach.^{55,59–61} They found out that most of the final structures of the boron clusters (n > 9) fell into two classes: (open-) spherical and convex/quasiplanar clusters. An "Aufbau principle"60 was proposed to construct various highly stable boron species using two basic units: the pentagonal pyramid B₆ and the hexagonal pyramid B_7 . Calculation results indicated that the B_7 cluster is the characteristic unit of convex and quasiplanar boron clusters, which can finally form boron nanosheets or boron nanotubes56,58 (Fig. 1). The pentagonal B_6 unit is the building block of stable bulk boron such as α-rhombohedra⁶² or tetragons.⁶³ Wang et al. experimentally proved the existence of planar or quasiplanar boron clusters by combined PES (photoelectron spectroscopy) experiment and theoretical calculation on boron clusters.⁶⁴ They thought that aromatic boron clusters have a more circular structure whereas antiaromatic boron clusters are elongated, analogous to structural distortions of antiaromatic hydrocarbons.

Similar to carbon nanotubes, theoretical simulations indicated that boron atoms form puckered hexagonal lattices in order to obtain a planar or quasiplanar boron sheet shape.^{56,58,65} The boron nanotube can be made of rolled-up pieces of the quasiplanar boron sheet.⁶⁶ Subsequent theoretical studies demonstrated that boron nanotubes showed a metallic-like density of state (DOS) and had high metallic conductivities irrespective of whether they have zigzag, armchair, or chiral structure.^{56,66} Very recently, Sorhrab Ismail-Beigi and Hui Tang presented a new



Fig. 1 Schematic diagram of the boron cluster growth according to the "Aufbau principle". One of the key elements is the hexagonal pyramid B_7 . Starting from one B_7 unit, further atoms are added to form new B_7 units, which finally leads to the formation of boron sheets and boron nanotubes. Reproduced from ref. 60, copyright (1997) The American Physical Society.

class of boron sheets, composed of triangular and hexagonal motifs, which are likely to be new precursors of boron nanotubes.^{67,68} The sheet was realized by removing an atom from a flat triangular sheet to produce a hexagonal hole, which showed a lower energy than any structure previously considered. Ni *et al.* have also predicted that the boron nanotubes rolled up from a novel flat boron sheet with symmetry of the triangular lattice are the most stable so far (Fig. 2).⁶⁹ After investigating the electronic and structural properties of these structures, they demonstrated that the boron sheet is a metal and the nanotubes can be either metals or semiconductors, dependent on their diameter and chirality.

3. The growth of boron nanostructures

3.1 Synthetic methods

In the past few years, various chemical and physical methods has been successfully used to synthesize 1D boron nanomaterials, such as nanowires, nanobelts, nanocones, and nanotubes. Here, we classified these methods into three categories: (1) chemical vapor deposition (CVD) with gas or solid precursors; (2) magnetron sputtering (MS); and (3) laser ablation (LA). Table 1



Fig. 2 A new precursor of boron nanotubes. (a) The structure of boron sheet and (b) the structure of boron nanotubes. Reproduced from ref. 69, copyright (1997) The American Physical Society.

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 Table 1
 Preparations of boron 1D nanostructure using different methods

Method	Morphology type	Procursor	Carrier gas	$T^{\circ}C$	Catalyst	Diameter /nm	Structure	Ref.
CVD^{a}	Nanowires	B, I ₂ , Si powder D U /A. (20/)	. v	1000–1100 1100	Au film Ni D	50-100 20-200	Amorphous	70
CVD	Nanotubes	$\mathbf{BCI_{3}}(\mathbf{H}, (2/0))$ $\mathbf{BCI_{3}}(\mathbf{H}, (1:6))$	H,	870	Mg-MCM-41	20-200 3	UIIKIIOWII CI YSIAI	99 99
CVD	Nanowires	$Ar/H_2/B_2H_6/(10:10:10\%)$	H_2^2	800	NČA	20-60	Tetragonal	85
CVD	Nanowires	B, I ₂ , Si powder		900-1200	Au film		Polycrystalline or rhombohedral	100
CVD	Nanoribbons	${ m B_2H_6/Ar/H_2(10:10:1\%)}$	Ar	630-750		20 - 100	Tetragonal	86
CVD	Nanowires	$B/B_2O_3(40wt\%)$		650-950	Au film	30 - 300	NWs bundle	71
CVD	Nanowires nanochains	$ m N_2/H_2/B_2H_6/(10:50:1\%)$	\mathbf{N}_2	750-1000	Au film	27	NWs,	98
							nanochains	
CVD	Nanowire Y-junction	$B/B_2O_3(40 \text{ wt}\%)$		1100-1200	Au film	30 - 130	Amorphous	72
CVD	Nanocones	B, B_2O_3	$H_2/Ar (5\%)$	1000 - 1100	Fe_3O_4 , B	50 - 100	α-Tetragonal	79
CVD	Nanowires	B, B_2O_3 , C	Ar	1000 - 1100	${\rm Fe_3O_4}$	20-40	α-Tetragonal	80
CVD	Nanowires	B, B_2O_3 , Mg	$H_2/Ar (5\%)$	1000 - 1200	$\mathrm{Fe_3O_4}$	50 - 200	β-Rhombohedral	81
MS^b	Nanowires	B/B ₂ O ₃ plate	Ar	500-800	Au film	10-20	Crystalline	92
MS	Nanowires	$B/B_2O_3(40wt\%)$	\mathbf{Ar}	800		40	Amorphous	88
							arrays	
MS	Nanowires	B target	Ar	800		40–60	Amorphous	91
SM	Feather-like Nanowires	B/B,O, target	Ar	800-900		20-40	arrays Amornhous	89.90
				0 0 0 0		62 - 2 1	arravs	
MS	Nanowires	$B/B_2O_3(40wt\%)$ target	Ar	annealed at 1050^d		15-60	β-Rhombohedral	76
\mathbf{LA}^{c}	Nanobelt	B pellet	Ar	700–900		50	a-Tetragonal	94
LA	Nanowires	B target	$H_2/Ar (5\%)$	$800/1300^{e}$		30 - 60	Amorphous	95
\mathbf{LA}	Nanowires	B/CoNi target	Ar	1250	CoNi	100	Tetragonal	93
LA	Nanowires	B, Ni Co and H ₃ BO ₃	Ar	1125-1500	NiCo	<100	Tetragonal	96
^{<i>a</i>} Chemical vaj	por deposition. ^b Radio frequen 20 min and then raised to 1300	icy magnetic sputtering. ^c Laser ab	lation. ^d BNWs was umina template.	prepared using CVD meth	od and then was annea	led in sealed tube a	ıt 1050 °C. [∉] The furnace v	was kept

summarized the reported synthesis conditions for 1D boron nanostructures by different methods.

3.1.1 Chemical vapor deposition (CVD). Chemical vapor deposition (CVD) is an effective and facile method to prepare one-dimensional nanostructures for both catalyst-free growth and catalyst-assisted VLS process. The first outcome of the experimental work on boron nanostructures used the CVD technique to synthesize amorphous boron nanowires. In this experiment, boron, iodine and silicon were introduced as precursors to synthesize amorphous boron nanowires at 1000-1100 °C, which may be used as the precursors to superconducting MgB₂ nanowires.⁷⁰ Yun et al. not only fabricated inclined a boron nanowires (BNW) bundle array, but also obtained a selfassembled BNW Y-junction by introducing an oxide-assisted VLS growth model.71,72 These boron nanostructures were synthesized on Si substrates which were coated with a 5-20 nm thick Au thin film as the catalyst by using a mixture of B, and B_2O_3 with proximately 40 wt% of B_2O_3 as the vapor source in the thermal vapor transport process. In past years, Gao's group have fabricated a variety of one-dimensional nanostructures using simple CVD techniques (Fig. 3).73-78 More recently, we also applied this technique to synthesize single crystal boron onedimensional nanostructures (nanocones and NWs) on the Si (111) substrate by thermal reduction of B and B₂O₃ at 900–1100 °C.^{79–82} In this process, we employed organic molecule capped-Fe₃O₄ nanoparticles⁸³ as catalyst, C, and Mg and Al powder as reducing agent. Using a mixture gas as the precursors and carrier gas in the CVD techniques is also an important way to synthesize boron nanostructures. Buhro et al. prepared boron nanowires with diameter of 20-200 nm at 1100 °C.84 In this typical experiment, the mixture gas of diborane (B_2H_6) and argon was the precursor, and NiB was catalyst. Yang et al. introduced a mixture gas of argon, hydrogen and diborane with a flow ratio of 10:10:1 in the furnace chamber by using nanochannel alumina (NCA) as the template to synthesize aligned single crystal boron nanowires at 800 °C without catalyst.⁸⁵ Xu et al. reported the catalyst-free growth of single crystal *a*-tetragonal boron nanoribbons by pyrolysis of diborane at a relatively low temperature and low pressure.⁸⁶ Boron nanowires on ZrB₂ particles were synthesized in a cold wall CVD system employing diborane as the B precursor and nitrogen as the carrier gas.⁸⁷ Morphology and diameter controllable boron nanowires were performed by using a mixed gas of nitrogen, hydrogen and diborane with a flow ratio of 10:50:1 using Au film as the



Fig. 3 Schematic of the chemical vapor deposition system. The carrier gas is (10%) H₂/Ar. The central part is the high temperature tube furnace. In the growth region, the precursor boat is 1.5 cm away from the substrate. The exhaust gas was pumped out by mechanical pump.

catalyst by controlling the reaction temperature and thickness of catalyst Au films.⁸⁷

3.1.2 Magnetron sputtering. The magnetron sputtering technique was one of the earliest techniques introduced to synthesis of boron nanostructures. Cao et al. firstly used Ar⁺ ions to sputter a target of boron and boron oxide mixture to synthesize self-assembly of boron nanofeather arrays without using templates or catalysts.^{88,89} Wang et al. also employed this radiofrequency magnetron sputtering method to prepare aligned boron nanowire arrays, with lengths up to tens of micrometres and diameters around 40-50 nm.90 Cao et al. further reported that well-aligned boron nanowires arrays were grown vertically on silicon substrates over areas up to several tens of square centimetres using radio-frequency (FR) magnetron sputtering of highly pure boron as the target using low RF power.⁹¹ Gao et al. reported that crystalline boron nanowires with a mean diameter around 10 nm and a typical length of several microns were successfully prepared using Si (100) as a substrate with Au catalyst and a simple radio-frequency magnetron process under argon atmosphere with Au catalyst.92

3.1.3 Laser ablation. The laser ablation technique is also a widely used way to grow boron-related nanostructures. Zhang et al. prepared single crystalline boron nanowires using a boron rod doped with 10 wt% of a 50 : 50 mixture of Ni and Co powder using a Nd/YAG laser with 532 nm wavelength, 10 Hz frequency and 3.5 W power.⁹³ Wang et al. reported on the synthesis of pure single crystalline tetragonal boron nanobelt with rectangular cross-section by the laser ablation technique with a third harmonic Nd:YAG laser (wavelength = 355 nm, pulse width = 5to 7 ns) on the target of boron pellet without using catalysts and at relatively low temperature and pressure.94 Meng et al. had successfully prepared amorphous boron nanowires by laser ablation in pressed boron targets at high temperature using the beam of a KrF excimer laser (Lambda Physik, Germany) with a wavelength of 248 nm and a pulse frequency of 10 Hz.95 Zhang and co-workers fabricated single crystalline boron nanowires on the surface of the targets by laser ablation using B/NiCo (or B/ H₃BO₃/NiCo) target with a pulsed, frequency-doubled Nd:yttrium-aluminium-garnet (YAG) laser (wavelength, 532 nm; repetition, 10 Hz).96

3.2 Controllable growth

3.2.1 Morphology and crystal structure control. Controllable growth of nanostructures' morphology and crystal structure is an essential way to control their physical properties and allow possible applications of nanomaterials. In the past few years, researchers have paid more attention to realize the growth of boron nanostructures with different morphologies and crystal structures (Fig. 4). Amorphous boron nanowires were first synthesized by CVD and magnet sputtering.^{70,88} Amorphous boron nanowires (Fig. 4A) are good precursors or candidates for preparing crystalline boron nanowires by annealing at high temperatures⁹⁷ or synthesis of other boron-related nanowires, such as MgB₂.⁷⁰ As we know, the crystal structures of bulk boron are diverse. Crystalline boron nanostructures with different crystal structures had been successfully and widely



Fig. 4 Novel boron nanostructures: (A) SEM image of amorphous boron nanowires, reproduced from ref. 70, copyright (2001) Wiley-VCH; (B), (C) SEM images of boron nanoribbons, reproduced from ref. 86, copyright (2004) American Chemical Society; (D) SEM image of single crystalline boron nanowires, reproduced from ref. 81, copyright (2008) American Institute of Physics; (E) TEM image of boron Y junction, reproduced from ref. 72, copyright (2006) American Chemical Society; (F) TEM image of boron nanocone, reproduced from ref. 79, copyright (2007) Wiley-VCH; (G) TEM image of boron nanotube, reproduced from ref. 99, copyright (2001) American Chemical Society.

reported by different groups. β-Rhombohedral boron nanowires were produced through post-annealing amorphous boron nanowires synthesized by RF magnetron sputtering.97 By introducing Mg to boron and boron oxide powder, Tian et al. directly synthesized β-rhombohedral boron nanowires on an Si substrate using Fe₃O₄ as the catalyst (Fig. 4D).⁸¹ Tetragonal boron nanowires with lattice parameters a = 0.875 nm, c =0.506 nm were synthesized by laser ablation with a higher (B/ NiCo) target temperature⁹³ than that of amorphous boron.⁹⁵ Tetragonal boron nanobelts or nanoribbons were also successfully produced by using laser ablation94 and CVD methods.86 In Fig. 4B and C, it can be seen that the boron nanoribbons show "grass like", "zigzag", and "palm-leaf like" structures. In the corresponding electron diffraction patterns and high resolution TEM images, the nanoribbons were demonstrated to be α-tetragonal boron. The growth of these nanoribbons is believed to be largely determined by the growth kinetics. Yun et al. demonstrated that boron nanowire Y-junction can be synthesized in a self-assembled manner by fusing two individual boron nanowires grown inclined toward each other.72 In this oxide-assisted vapor-liquid-solid (VLS) process, the lowmelting B₂O₃ was present during BNW growth. Nanocones are considered to be ideal field emission electron sources that can emit electrons at low electric field due to their nanoscale and special geometry (small curvature radius). a-Tetragonal boron nanocones were also successfully fabricated in Gao's group (Fig. 4F) using boron powder and Fe₃O₄ NPs as co-catalysts.⁷⁹ By controlling the growth temperature and the thickness of catalyst Au films, Yang et al. successfully realized morphology and diameter control on boron nanowires by means of chemical vapor deposition on silicon substrates using N2/H2/B2H6/ (10:50:1%) as the precursors.⁹⁸ Finally, the only work on synthesis of single-walled boron nanotubes with diameters in the range of 3 nm (Fig. 4) was reported,99 a breakthrough which

could open a whole new field in nanotechnology based on compound nanotubular networks.

3.2.2 Position control. To realize the alignment growth of nanostructures the typical techniques are using templates or patterned catalysts. Cao and co-workers synthesized boron nanowire and nanofeather arrays in an argon atmosphere by a simple method of magnetron sputtering using a target of highly pure boron (Fig. 5A and B).88,91 Their results suggest that this approach may be an economically feasible way to form a large variety of self-organized nanostructures exhibiting desirable assemblies. Yun et al. investigated the effects of quenching on the BNWs' crystallinity and alignment in BNW films fabricated in the thermal vapor transfer process (Fig. 5D).¹⁰⁰ They have found that quenching can remarkably enhance both the crystallinity and alignment of the BNW grown on Si substrates when processing temperatures were >1100 °C. The BNWs formed at temperatures >1100 °C are polycrystalline with a rhombohedral structure while lower temperature processed BNWs are amorphous. If higher-temperature processing is followed by a quenching, predominant single-crystalline BNW arrays of (031) orientation aligned with the normal of the substrates can be obtained. As we know, templating is a common method used for growth of nanostructure arrays. Yang et al. reported the well aligned boron nanowires (BNWs) with single crystalline structure were successfully prepared by using nanochannel-Al₂O₃ template (AAO) as a substrate and a chemical vapor deposition process without using any metal catalyst at the temperature of 800 °C (Fig. 5E).85 Recently, Liu et al. used C, B and B₂O₃ powders as precursors and Fe₃O₄ nanoparticles as catalyst to synthesize BNWs arrays via the above-mentioned CVD growth process at atmospheric pressure. High density and single crystal BNWs arrays were grown vertically on the Si (001) substrate (Fig. 5C and F).80



Fig. 5 Boron nanostructure arrays: (A) feather-like armorphous boron nanowires, reproduced from ref. 88, copyright (2001) Wiley-VCH; (B) armorphous boron nanowires, reproduced from ref. 91, copyright (2002) American Institute of Physics; (C), (F) crystalline boron nanowires, reproduced from ref. 80, copyright (2008) Wiley-VCH; (D) crystalline boron nanowires, reproduced from ref. 100, copyright (2004) American Institute of Physics; (E) crystalline boron nanowires with templates, reproduced from ref. 85, copyright (2003) Elsevier Science B. V.

The fabrication of patterned nanostructures for applications including nanoelectronics through display units, information storage devices, micro-optical components, and miniaturized sensors has had a great deal of interest in the past few years.^{101–103} To date, much effort has been focused on the synthesis and patterning of nanoparticles by lithography, using either photon, electron/ion-beams, or other high energy particles. In Gao's group we developed a very simple and direct methodology to pattern Fe₃O₄ nanoparticles on an Si(111) surface by the self-assembly

technique. Fe₃O₄ nanoparticles were synthesized by a simple high temperature solution phase reaction technique.⁷¹ To realize self-assembled Fe₃O₄ nanoparticles on Si(111) wafer the concentration, dosage of the solution, and temperature of the substrate has been well controlled. Fe₃O₄ nanoparticles of uniform size have been used as a catalyst to synthesize one-dimensional 1D nano-structures.^{76–78} The patterned Si wafers (Fig. 6A–C) were subsequently used as substrates to grow patterned boron nanowires (Fig. 6D–I) *via* a simple chemical vapor deposition.⁸²



Fig. 6 (A–C) The SEM images of assembled Fe_3O_4 nanoparticles on silicon substrate; (D–I) The SEM images of patterned boron nanowires grown on the substrate. Reproduced from ref. 82, copyright (2009) American Institute of Physics.

4. Potential applications

4.1 Electric transport

The ordered crystal structures of boron are built on a B_{12} icosahedral unit and include *a*-rhombohedral, *a*-tetragonal, and β-rhombohedral units.^{54,84} The conductivity of bulk boron varies from 10^{-4} to 10^{-7} (Ω cm)⁻¹ due to its crystal structure variety. The first theoretical predcation of the transport properties of boron nanostructures was carried out by P. Pandey and co-workers.57 They calculated the I-V characteristics of (6,0) and (0,6) single wall boron nanotubes (SWBNTs) using a tight-binding approach and the Landauer-Büttiker multichannel formalism. The conductivity in SWBNT is predicated to be higher than that in single wall carbon nanotubes (SWCNT) and the chirality of boron nanotubes does not appear to play a significant role in determining the I-V characteristics of a BNT. They claimed that it is attributed to a mixture of localized two-center bonds and delocalized multicenter electron-deficient nature of boron bonds in SWBNT. Following this, they also found that the differential conductance and the tunnel current for B-fullerenes sandwiched between Au contacts are much higher than those for C_{60} , which is due to metal-like states, formed from the hybridization of Au 6s orbital with the highest occupied molecular orbital of B-fullerenes delocalized over the equator of the icosahedral cages.¹⁰⁴ Due to their predicted enhanced electron transport properties, B nanostructures appear to be attractive candidates for future nanoscale electronics. These predictions also stimulated great interest in experimental measurement of the conductivities of 1D boron nanostructures. If the experimental results are consistent with what has been predicted, 1D boron nanostructures will be very promising as building blocks for the next generation of nanoelectronic devices.

An early measurement was carried out on the boron nanowires with diameters of 46, 115, and 58 nm, however, without identifying their crystal structures. The conductivity was measured using two PtIr probe tips in the SEM,⁸⁴ and it came out on the order of $10^{-5} (\Omega \text{ cm})^{-1}$. This work was then followed by building two boron nanowire devices using Ni and Ti as contact electrodes by electron-beam lithography.¹⁰⁵ Because boron is a p-type semiconductor, Ni electrode had a good Ohmic contact to boron nanowires, while Ti electrode had Schottky-barrier contacts. The conductivity of a single boron nanowire with an average diameter of 60 nm was measured at the order of $10^{-2} (\Omega \text{ cm})^{-1}$ after annealed at 400 °C for 10 min. It turned out a fourfold increase over the conductivity of β -rhombohedral bulk broron. Thermal treatment led to an improvement of the interfacial contact between the electrodes and the boron nanowire.

The room temperature conductivities of boron nanobelts with α-tetragonal structure were reported by Kirihara et al.^{106,107} It was demonstrated that the conductivities of boron nanobelts were improved to $2.5-4.5 \times 10^{-3} (\Omega \text{ cm})^{-1}$ by Mg doping and it was proportional to the operating temperature. The theoretical study and some experimental results suggested that the conductivity of bulk boron can be improved by appropriate carbon doping. In the unit cell of *α*-tetragonal boron, there are several interstitial atomic sites that can accommodate some adventitious atoms. The electronic transport of Mg-doped boron nanobelts was found to be 2.8×10^{-1} (Ω cm)⁻¹ at 290 K, which was hundred of times higher than pure boron nanobelts. The Mg atoms occupying the interstitial sites donate electrons to the densely distributed intrinsic acceptor levels in a rigid band scheme. It might lead to the high value of $N(E_{\rm F})$ (the electron density of localized state at the Fermi level) and thus improved the overall conductivity of nanobelts. This section focuses on the recent progress on experimental measurement of electric transport in single crystalline boron 1D nanostructures.

4.1.1 Boron nanocones. In one of our previous works, the electronic transport properties of α-tetragonal structured boron nanocones were measured.⁷⁹ Three experimental devices were designed for the conductivity measurement at room temperature. Fig. 7 shows SEM images of three devices with different sized boron nanocones. The boron nanocones used in each device were 110–190 nm \times 3.1 μ m (top-root and length, device 1, Fig. 7A), 240–280 nm \times 3.8 μ m (device 2, Fig. 7B), and 450 nm \times 2.5 μ m (device 3, Fig. 7C), respectively. All the electrodes were fabricated by depositing Ni/Au at the ends of nanocones using electron-beam lithography. Fig. 8 illustrates room temperature current-voltage (I-V) curves of the above three devices in the voltage range of -20 V to 20 V. The inset represents I-V curves in the small voltage range of -1.0 V to 1.0 V. The I-V curve for Device 3 is symmetrical. The current increases linearly from -60pA to 60 pA as voltage is raised from -1.0 V to 1.0 V and the conductivity is calculated to be about $1.0 \times 10^{-5} (\Omega \text{ cm})^{-1}$. The current saturates with further increasing the voltage above 1.0 V and decreasing the voltage below -1.0 V. Similar saturation tendencies are also found for Device 1 and 2. But, their curves are not symmetrical in shape. For Device 1 and 2, conductivity is not concord calculated by positive and negative current because the diameter of top and root of nanocones are different. The



Fig. 7 SEM images of three boron nanocone devices with different diameters and lengths connected with Au electrodes. (A) Device 1 (length, 3.1 μm, the diameters of both ends, 110 nm and 190 nm); (B) Device 2 (length, 3.8 μm, diameters of both ends, 240 nm and 280 nm); (C) Device 3 (length, 2.5 μm, diameters of both ends, 450 nm). Reproduced from ref. 79, copyright (2007) Wiley-VCH.



Fig. 8 Room temperature current–voltage (I-V) curves of three devices at the voltage range of -20 V to 20 V, the inset is I-V curves at small voltage range of -1.0 V to 1.0 V. Reproduced from ref. 79, copyright (2007) Wiley-VCH.

conductivity values of $1.0-7.3 \times 10^{-5}$ (Ω cm)⁻¹ observed here are ten times greater than that of pure bulk boron.¹⁰⁸ It is consisted with what has been observed in pure boron nanowires,⁸⁴ and lower than that of those metal-doped 1D boron nanostructures¹⁰⁶ and carbon-doped bulk boron.¹⁰⁷ The asymmetric I-V curves for Device 1 and 2 are attributed to the intrinsic character of boron nanocones. The boron nanowires and nanobelts with uniform size in whole length have the same carrier concentration and carrier mobility at the same positive and negative voltage, leading to the same export currents.¹⁰⁶

Device 3 with comparative diameter size of both ends has the similar I-V curve shape with that of boron nanowires. The velocity excursion of carriers of boron nanocones for Device 1 and 2 is different at the same positive and negative potentials due to the diameter size distinctness along the cones, which results in the variety of carrier mobilities and thus led to the different saturation currents.

4.1.2 Boron nanowires. The electric conductivity of boron nanowires was first measured on polycrystalline boron nanowires using PtIr electrodes in SEM.84 To measure the conductivity of single crystalline boron nanowires, we designed four devices using β-rhombohedal boron nanowires as model materials.⁸¹ The contact electrodes of Device 1 were fabricated by electron beam lithography using four Ni/Au Ohmic contacts (Fig. 9A). For comparison, Pt Ohmic contact electrodes on boron nanowires (Devices 3 and 4) were fabricated by focused ion beam. Fig. 9B shows a typical SEM image of the devices fabricated by a focused ion beam. The four devices were measured in a four-probe scanning tunneling microscope (STM) system. Fig. 10A shows I-V characteristics of single boron nanowire in Device 1 measured at different operating temperatures. All the I-V curves are linear and symmetrical under a bias voltage of up to 4 V, and the conductance increases with the temperature. The conductivity at 460 K is a thousand-fold increase over the conductivity at 120 K, which indicates that the single-crystalline boron nanowires are good semiconductors above room temperature. Such positive temperature coefficient phenomena were also observed in polycrystalline ZnO varistors¹⁰⁹ and Cd-doped ZnO nanowires.¹¹⁰ The electrical



Fig. 9 Typical SEM images of a boron nanowire device made by electron beam lithography (EBL) (A) and a nanowire device fabricated by focused ion beam (FIB) (B).



Fig. 10 (A) The *I–V* characterization of a boron nanowire. (B) Temperature dependence of electrical conductivities of four different devices. The indexed numbers of each curve represent the corresponding devices. Reproduced from ref. 81, copyright (2008) American Institute of Physics.

conductivity of this Device 1 is about $4.4 \times 10^{-4} (\Omega \text{ cm})^{-1}$ at room temperature, which is close to the value of bulk boron.¹⁰⁸ For comparison, Device 2 was made by electron beam lithography and mended by a focused ion beam at the contacts between the nanowire and electrodes. The conductivity of Device 2 is $3.6 \times 10^{-2} (\Omega \text{ cm})^{-1}$, showing a hundread-fold increase over Device 1. The same behavior was also observed in Device 3 and 4. This increasing behavior of conductivity on the three devices mended by a focused ion beam is probably due to the doping effect of adventitious atoms from electrodes during the focused ion beam process.

Fig. 10B gives linear relationships between Ln(G) and $(1/T)^{1/4}$ of these four devices. Here, *G* is the conductivity and *T* is the temperature. Such linear dependence fits in with Mott's variable range hopping (VRH) model, assuming that the carrier transport occurs by thermal activation process between the localized states.

 β -Rhombohedral B
(polycrystalline) β -Rhombohedral B (single crystal)Device 1Device 2Device 3Device 4 T_0/K 5.1×10^9 8.7×10^7 6.8×10^7 2.56×10^7 2.47×10^7 5.4×10^7

Table 2Model parameter T_0 of Mott's VRH model. Reproduced from ref. 81, copyright (2008) American Institute of Physics

According to Mott's law of three-dimensional VRH, the conductivity G can be expressed as,

$$G = G_0 \exp\left\{-\left(\frac{T_0}{T}\right)^{1/4}\right\}$$
(1)

$$T_0 = \frac{60}{\pi k_{\rm B} l^3 N(E_{\rm F})}$$
(2)

where *l* is the localization length of the carrier's wave function, $N(E_{\rm F})$ is the electron density of localized states at the Fermi level $(E_{\rm F})$, $k_{\rm B}$ is the Boltzmann constant, and G_0 is a constant. The corresponding fit parameters T_0 of the temperature range are listed in Table 2. The conductivities measured on single crystalline β -rhombohedal boron nanowires matched well in this model.

It is interesting that the conductance of single crystal boron nanowires is very robust even under large strain. In the experiment, one end of an individual boron nanowire was fixed by a Pt electrode through focused ion beam operation. One Au tip in the four-probe STM system was used as an electrode in a twoterminal configuration as well as the nanowire manipulator. As illustrated in Fig. 11, the electrical conductance measurement was monitored during the process of bending the nanowire.⁸¹ The mechanical strain the nanowire experienced can be quantized as ε = r/R, where r and R represent the nanowire's radius and the radius of curvature, respectively. The nanowire remains intact even after 3% strain bending and manifests excellent resilience (Fig. 11C). The conductivity of boron nanowire persisted while increasing the strain gradually. The measured resistivities for each step in Fig. 11A-C are 139.3, 143.8, and 142.4 Ω cm, respectively. After plotting the data of $\ln(G)$ versus $(1/T)^{1/4}$ with and without mechanical strain (Fig. 12), it was found that the electrical conductivity is independent on mechanical strain. It is similar to the one without mechanical strain. It indicates that the strain applied on the boron nanowire did not change the electron



Fig. 12 Temperature dependence of conductivities of nanowires with and without mechanical strain. Reproduced from ref. 81, copyright (2008) American Institute of Physics.

density of localized states at the Fermi level. This finding demonstrated that the single crystalline boron nanowires are very promising as building blocks for flexible nanoelectronic devices.

4.1.3 Boron nanobelts. The electric conductivities of pure and Mg-doped single crystalline boron nanobelts were measured by Kirihara *et al.* using two Au/Ni electrodes.^{106,107} The boron nanobelts were firstly dispersed in dehydrated ethyl acetate and dropped onto a surface oxidized silicon wafer. Then Ni/Au electrodes were made at the two ends of the nanobelt by electron beam lithography. Fig. 13 shows SEM images of so-fabricated boron nanobelt devices for conductivity measurement. The selected boron nanobelts were 25 nm in thickness and 100 nm in width. The *I–V* curves of a single pure boron nanobelt and a single Mg-doped boron nanobelt at 290 K were compared in Fig. 14. The curve of the Mg-doped boron nanobelt was symmetrical and linear, indicating the Ohmic contacts between



Fig. 11 SEM images of a single boron nanowire under a mechanical bending process. Reproduced from ref. 81, copyright (2008) American Institute of Physics.



Fig. 13 SEM images of boron nanowires after Ni/Au electrode fabrication. (A) A pure boron nanowire; and (B) a Mg-doped boron nanowire. Scale bar is 2 µm. Reproduced from ref. 107, copyright (2005) American Vacuum Society.



Fig. 14 *I–V* characteristics of a pure boron nanobelt and a Mg-doped boron nanobelt measured at 290 K. Reproduced from ref. 107, copyright (2005) American Vacuum Society.

the nanobelt and the electrodes. The slope of Mg-doped I-Vcurve was much steeper than that of the pure boron nanobelt after Mg vapor diffusion. The measured electric conductivities at 290 K for pure boron nanobelts and Mg-doped ones were 2.2 \times 10^{-3} (Ω cm)⁻¹ and 2.8×10^{-1} (Ω cm)⁻¹, respectively. The doped nanobelt showed a hundred-fold increase in electric conductivity over the pure one. The temperature dependence of conductivities of the pure and doped boron nanobelts was also studied at the same time by Kirihara et al.¹⁰⁷ They found that both pure and doped nanobelts exhibited semiconductor behavior. Their slopes of I-V curves increased with increasing temperature. A very small current was recorded at 34 K for the Mg-doped boron nanobelt and this low temperature is lower than the transition temperature of superconductor MgB₂.¹¹¹ It indicates that there was no MgB₂ formed in the boron nanobelt and Mg was indeed doped in the boron. In addition, the temperature induced slope change of *I*-V curves of the Mg-doped nanobelt was slower than that of the pure boron nanobelt. This feature indicates that temperature coefficient of electric conductance was not significant in the doped boron nanobelt. The conductivity increase observed on the Mg-doped boron nanobelt was ascribed to the occupation of the interstitial sites by Mg atoms or trace Si atoms, which donated electrons to the densely distributed IALs in a rigid band scheme and thus resulted in a high value of $N(E_{\rm F})$.¹⁰⁷

4.2 Field emssion

Metal or semiconductor 1D nanostructures such as nanotubes and nanowires have been well accepted as ideal field emission electron sources for emitting electrons at low electric field due to their nanoscale and special geometry (high aspect ratio and lower curvature radius).^{43,112,113} A good emitter material for field emission requires not only a low turn-on voltage, but also a high durable emission current. It needs some properties, such as small electron affinity, low work function, high aspect ratio, high thermal stability and better mechanical strength at high temperature. In the past decade, a lot of materials including Spindt-tip arrays,¹¹⁴ low electron affinity III–V nitride nanocones/nanowires,^{115,116} diamond films,¹¹⁷ transition metal oxide nanowires,^{118–121} and carbon nanotubes^{122–124} have been systemically studied as field emitters. Among these nanostructures, carbon nanotubes were well-recognized as one of best field emission materials. However, due to their poor emission stability and low melting point, carbon nanotubes are limited in building field emission devices. This section reviews the field emission properties of single crystalline boron 1D nanostructures. Compared to other materials, the nature of boron offers its 1D nanostructures many advantages, such as a high melting point ensuring long-term stability, low-electron-affinity-induced largefield emission current density, and strong mechanical strength, resulting in high mechanical performance.

4.2.1 Boron nanocones. The field emission properties of boron nanocones were studied using a boron nanocone thin film on silicon substrate. Fig. 15 shows its current density versus the electric field J-V characteristics.⁷⁹ The turn-on electric field and the threshold electric field were defined as 10 μ A cm⁻² and 1 mA cm⁻², respectively. For boron nanocones, low turn-on and threshold electric fields were found at 3.5 and 5.3 V μm^{-1} , respectively. The emission current density was increased to 25 mA cm⁻², with no saturation tendency as the electric field was increased to 12 V μ m⁻¹. The *J*–*V* relationship was analyzed by the Fowler-Nordheim (F-N) function and the corresponding F-N plot is shown in the inset of Fig. 15. It exhibits a nonlinear behavior in the measurement range of 0.07–0.30 μ m V⁻¹. The $\ln(J/E^2)$ versus 1/E curve could be approximately divided into three regions for these boron nanocones. Region 1 refers to a low electric field, where field emission mainly depends on the surface states. With increasing the electric field, the surface potential barrier decreases and the current increases rapidly. In Region 3, the field penetration breaks down the surface potential barrier to dominante the field emission. Region 2 is a transition state between Region 1 and 3. It shows a competition between the surface states and the field penetration. In addition, high stability at a high emitting current was also found in these boron nanocones. An average emission current density of 25 mA cm⁻² was set at a constant electric field of 12 V μm^{-1} and its fluctuations were recorded over 12 h. The fluctuation of the current density was less than $\pm 3\%$ and no remarkable degradation was found during the measurement.



Fig. 15 Field-emission J-V curve of boron nanocones and corresponding F–N plot, which is divided into three regions (inset). Reproduced from ref. 79, copyright (2007) Wiley-VCH.

4.2.2 Individual boron nanowire. We first measured the field emission properties of an individual boron nanowire using a modified high vacuum SEM system.⁸⁰ As illustrated in Fig. 16, the tungsten probe was moved to contact an individual boron nanowire and the resistance along the nanowire was recorded by a pico-amperemeter. The detected voltage on the probe was -5 Vat this step to ensure the alignment as well as the Ohmic contact between the probe and the nanowire. The tungsten probe was then retracted to a distance from the boron nanowire by a stepped motor. As the probe left the boron nanowire, the voltage from the pico-amperemeter returned to zero. The field emission current was recorded as a function of the applied voltage up to 200 V in steps of 0.5-1 V. By measuring many nanowires individually, there were three representative curves of current versus electric field (I-E) as shown in Fig. 17A. A stable field emission current of 1µA was reached under the applied electric field between 59 and 74 V μ m⁻¹. The calculation based on this result gave a maximum emission current density of 2×10^{5} -4 $\times 10^{5}$ A cm⁻², which indicates boron nanowires may be a promising candidate as high-brightness point electron sources.

It is noticed that these three representative field emission behaviors exhibited slight differences. Nanowire a showed the best behavior although there was no remarkbale morphology difference among the three nanowires. To explore the details of field emission behavior, the conductivity of these three typical nanowires was also measured and plotted in Fig. 17B. Through this measurement, it was found that the three nanowires process different electrical conductivities. Nanowire a and c showed the highest ($8 \times 10^{-3} (\Omega \text{ cm})^{-1}$) and the lowest ($3.2 \times 10^{-3} (\Omega \text{ cm})^{-1}$) conductivities, respectively. It is probably the difference in conductivity that results in the difference in field emission behavior. These results suggested that the field emission performance of an individual boron nanowire seems proportional to its electrical conductance. The measured field emission featured a behavior up to 4 μ A without breaking down, which is very



Fig. 16 SEM images of the single boron nanowire during FE measurements. SEM images of the W probe and the single nanowire (A) before and (B) during the measurement. Reproduced from ref. 80, copyright (2005) Wiley-VCH.



Fig. 17 (A) The current-electric field (I-E) curves of individual boron nanowires: a–c refer to the three different boron nanowires. (B) The corresponding current–voltage (I-V) curves of these three individual boron nanowires (a–c) in FE measurements. Reproduced from ref. 80, copyright (2005) Wiley-VCH.

encouraging compared to the best results obtained from other nanowires.¹²⁵⁻¹²⁷

4.2.3 Boron nanowire arrays. The successful synthesis of aligned boron nanowires in a large scale provided us the opportunity to measure the field emission behavior of boron nanowire arrays.⁸⁰ Fig. 18A shows the field emission curve of current density versus electric field (J-E) from large-area boron nanowire arrays. The turn-on electric field (E_{on}) and the threshold electric field (E_{thres}) of the nanowire arrays are 5.1 V μm^{-1} (J = 10 $\mu A \text{ cm}^{-2}$) and 11.5 V μm^{-1} (J = 1 mA cm⁻²), respectively. Increasing the electric field to 17.8 Vµm⁻¹ resulted in a higher current density of 8.1 mA $\rm cm^{-2}$ without the saturation tendency. The E_{thres} value of the boron nanowire arrays is higher than that of carbon nanotubes $(1.6 \text{ V} \,\mu\text{m}^{-1})^{128}$ and tungsten oxide nanowires (6.2 V µm⁻¹).¹²⁹ Since nanowire arrays in a very high density are often harmful to field electron emission due to screening effects,^{130,131} attempts were made to control the density of these vertical boron nanowire arrays to fit in with the optimized theoretical values.132,133 Fig. 18B is the FN plot of the arrays of aligned boron nanowires. The FN plot is almost linear, agreeing well with the FN theory. However, the field emission behavior of the boron nanowire arrays at high current density is different from that of an individual boron nanowire. This is probably because the proportion of the thermal electron current for arrays in the measured field-emission current at high current density is too small to contribute to the FN plot. Since the field emission behavior of boron nanowire arrays was studied on a high density nanowire film, it partially concealed the true field emission properties of boron nanowires and thus a clear understanding on its field emission mechanism is still desirable.



Fig. 18 (A) The *J*–*E* field-emission curve of a large-area film of vertically aligned boron nanowires. (B) FN plot of this sample. Reproduced from ref. 80, copyright (2008) Wiley-VCH.

4.2.4 Patterned boron nanowires. Since a high density of nanowire arrays may lead to screening effects during field emission, patterned field emission materials with a controlled interval distance on a substrate have attracted great attention in the fabrication of display units. As presented in the method section, we have successfully fabricated patterned boron nanowires using a catalyst patterned silicon substrate.⁸² The distance between these boron nanowire patterns were about 20-30 µm and each pattern was 10-15 µm in diameter. In the measurement, the vacuum gap between the boron nanowires and Mo tip was 300 μm under a pressure of 2 \times 10⁻⁶ Pa. Fig. 19 shows the field emission curve of current density versus electric field (J-E) from the patterned boron nanowires. The turn-on field is 15 V μm^{-1} (defined as the applied field of 10 μ m cm⁻¹) and the apparent threshold field is 24 V μ m⁻¹ (defined as the applied field of 1 mA cm^{-2}). The measured turn-on field is higher than that of boron nanocones, but still lower than other field emission materials,



Fig. 19 Typical field emission characteristics of the patterned boron nanowires. Reproduced from ref. 82, copyright (2009) American Institute of Physics.

such as AlN nanocones¹³⁴ and nanowires.^{135–137} This moderate turn-on field might be ascribed to the fact that the distance between each pattern is larger than the distance for the most effective electron emission. It has been well-accepted that the most effective nanowire emitters usually have their ratio of the interval distance to the nanowire length close to 1. In this case, the distance between each pattern is $20–30 \ \mu\text{m}$ and the length of boron nanowires is about $5 \ \mu\text{m}$, giving a ratio of 4–6. The high density of boron nanowires on each pattern probably also resulted in a screening effect. In addition, the random orientation of the nanowires also partially contributed to the moderate turnon field.⁸²

Conclusions and outlook

Recent advances in the dynamic area of boron nanostructures have been drafted in this review paper. Recently, various 1D boron nanomaterials, such as nanowires, nanobelts, nanocones and nanotubes have been successfully synthesized by chemical and physical methods. We classified these methods into three categories: 1) chemical vapor deposition (CVD) with gas or solid precursors; 2) magnetron sputtering; and 3) laser ablation. Several technical approaches for fabricating high density boron 1D nanostructure arrays and patterned nanostructures were also discussed. Although significant progress has been made on controlled growth of 1D boron nanostructures, a breakthrough in terms of highly ordered arrays, large scale synthesis, patterned growth, morphology control as well as simplifying current recipes is still highly desired. In particular, the controlled synthesis of boron nanotubes currently is a focus area to be developed since the theoretical studies have predicted a high electric conductivity of boron nanotubes, which are promising to exhibit even higher electric conductivity than carbon nanotubes.56,58 To date, only one attempt was successful on the synthesis of boron nanotubes by employing Mg-MCM-41 as template⁹⁹ and the progress on high quality, large scale or highly crystalline boron nanotubes as well as the transport measurements on these novel structures remained blank in this field. More efforts from the experimental community are still required to develop new methods not only to synthesis novel nanostructures (such as nanotubes and fullerenes) but also to run measurements on the conductivity of these nanostructures. To verify these theoretical predictions of boron nanostructures experimentally is not only fundamentally interesting, but also appealing for the discovery of new generation nanodevices.

The two main physical properties of 1D boron nanostructures are electronic transport and field emission, which are quite interesting as they give 1D boron nanostructures great potential for field emission, flexible displays, superconductors, energy storage, and nanoelectronic devices. However, like most popular 1D nanomaterials, there are still many key scientific problems to be understood for their true application. One aspect is the relationship between the transport properties and crystal structures of boron. Boron has several different crystal structures. It is important to study the transport properties of boron nanostructures with different crystal structures. Moreover, more effort should be devoted to understand the transport mechanism by varying the measurement conditions, such as temperature, strain, and doping. For field emission applications, more attention may be paid to both synthesis techniques and property measurements. Boron nanostructures with uniform size, proper density, and/or a controlled interval distance are highly essential to enhance the properties of field emission. In addition, to realize flexible displays, flexible and conductive substrates for growing boron nanostructures are also highly desired.

There are almost unlimited research opportunities that are being and will be explored by researchers in this dynamic area. By understanding these scientific and technical issues, we believe that 1D boron nanostructures will continue to give exciting results toward their application.

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