

Do all wurtzite nanotubes prefer faceted ones?

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First-principles computations have been performed to investigate the stability of one-dimensional (1D) crystalline nanowires, faceted nanotubes, and conventional single-walled nanotubes (SWNTs) with various sizes, as well as the two-dimensional infinitely single layers for several wurtzite materials. Regardless of the diameters, the SWNTs are more stable than sp^3 -dominated faceted nanotubes and nanowires for BN and C, while for AlN, GaN, ZnO, ZnS, and Si, the faceted nanotubes and nanowires are always more preferred energetically than SWNTs. However, the stability of SiC SWNTs relative to other 1D nanostructures is diameter-dependent: the SiC SWNTs are more stable than thinner faceted nanotubes and nanowires, but less stable than thick ones. This indicates that SiC SWNTs and faceted nanotubes/nanowires preserving wurtzite configuration can coexist in nanoscale. The different stabilities for various nanostructures are attributed to the competition between sp^2 and sp^3 hybridization of the atoms in wurtzite materials associated with the difference in the atomic radius and electronegativity of the elements involved. © 2009 American Institute of Physics. [DOI: 10.1063/1.3140099]

I. INTRODUCTION

Inspired by the structural elucidation of carbon nanotubes in 1991,¹ one-dimensional (1D) nanostructures have been attracting great research interest for their unusual properties and potential applications, associated with their low dimensionality, quantum confinement effect, and boundary effect. Naturally explorations of nanotubes were first extended to other layered materials. Many layered compounds, such as metal dichalcogenides MoS₂,² WS₂,^{2(a),3} TiS₂,⁴ ZrS₂ and HfS₂,⁵ metal halide NiCl₂,⁶ and BN,⁷ were folded into nanotubes.⁸ All the above mentioned layered materials have no strong interlayer bonds and the layers are held together by van der Waals interaction; therefore, it is easy to understand that these compounds can be rolled into cylindrical form under certain conditions. However, some nonlayered materials, especially wurtzite crystals such as GaN (Ref. 9) and AlN (Ref. 10) also exhibit tubular morphologies, though they resemble their bulk phase rather than single-walled nanotubes (SWNTs).

Wurtzite structure is adopted by many crystals, such as BN, Si, SiC, AlN, GaN, ZnO, and ZnS. All these materials have wurtzite structure as the stable phase except BN, which crystallizes in cubic and hexagonal phases. However, hexagonal BN can transform into wurtzite structure under high pressure. A wurtzite structure can be seen as nonlayered or layered with strong interlayer interaction. Atoms in wurtzite crystals, except for the surface atoms, are all fourfold-coordinated with tetrahedral configurations

In recent years, wurtzite nanostructures, especially nanotubes, have been well studied for their promising applications in electronic devices, such as optoelectronics and biochemical sensors. Initially, single-walled carbon nanotubelike structures were assumed for these inorganic nanotubes. Theoretical studies on GaN,¹¹ AlN,¹² ZnO,¹³ and ZnS (Ref. 14) demonstrated that the SWNTs of wurtzite materials are rather stable since the strain energies of these tubes are lower than those of BN and carbon nanotubes. The silicon SWNTs and nanowires were also investigated theoretically.¹⁵

However, these SWNTs are rather artificial and hypothetical. Goldberger *et al.*⁹ synthesized the single-crystalline GaN nanotubes using ZnO nanowires as templates; Wu *et al.*¹⁰ synthesized the single-crystalline *h*-AlN nanotubes without templates. Instead of the layered tubular structure and smooth tube walls, they found that the as-obtained AlN nanotubes have the faceted geometry with hexagonal cross sections. Via the thermochemistry process, Yin *et al.*¹⁶ successfully synthesized the highly faceted wurtzite-type single-crystalline ZnS nanotubes also with hexagonal cross sections. Among several experiments to synthesize Si nanotubes,^{17,18} none has achieved the SWNT structure. By means of density functional theory (DFT) computations, several groups showed that the Si nanotubes prefer puckered structures instead of smooth tubes,¹⁹ and Chen *et al.*²⁰ verified that the faceted model of AlN nanotube is energetically more favorable than the cylindrical one, which was also confirmed by others.²¹ The following theoretical studies demonstrated that the faceted tube models are also favored by GaN,²² ZnO,²³ ZnS,²⁴ and Si.²⁵ To our best knowledge, the single-walled AlN, GaN, ZnO, ZnS, and Si nanotubes are

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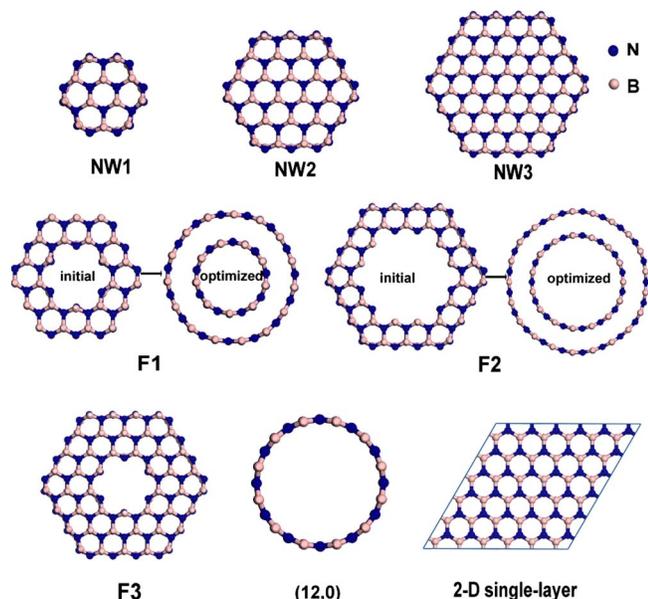


FIG. 1. (Color online) Top view of atomic configuration of BN nanostructures. Both initial and optimized structures for BN faceted nanotubes F1 and F2 are also given. Moreover, the nomenclature of BN nanostructures is also applicable to other wurtzite materials considered in this work.

still hypothetical materials up to now. Does this mean that the cylindrical forms of wurtzite materials are all impossible?

The answer is absolutely *no*. Sun *et al.*²⁶ reported the formation of SiC nanotubes by reacting silicon with multiwalled carbon nanotubes (also as templates). The produced SiC nanotubes are multiwalled with 3.5–4.5 Å interlayer spacing, indicating that coupling between the layers is quite slight and each layer can be considered as a SiC SWNT. This finding is quite remarkable since bulk SiC has no layered structure as graphite and *h*-BN, which also stimulated the theoretical investigations on SiC SWNTs.²⁷ Hence one question arises: why can SiC form the single-walled tubular structure while other wurtzite materials cannot? In this paper we report the evolution rule of nanostructures of wurtzite materials, including BN, Si, AlN, GaN, ZnO, ZnS, and SiC, to address the above question by means of DFT computations. Several structures, including nanowires, faceted nanotubes, and SWNTs with different sizes as well as two-dimensional (2D) infinite single layer were considered for each wurtzite material, and the corresponding carbon nanostructures were also studied for comparison.

II. COMPUTATIONAL METHODS

In this work, crystalline nanowires and faceted nanotubes with various sizes were compared with conventional SWNTs and 2D infinite single layers. The models of hexagonal single-crystal nanowires and faceted tubes were constructed from the experimental wurtzite structures, as exemplified by BN in Fig. 1. First, a large bulk supercell is constructed, and then the initial models of several crystalline nanowires and faceted nanotubes of different sizes are obtained by cutting the supercell with cylinders of various diameters. The atoms outside the cylinder are removed to

achieve crystalline nanowires with different diameters. The atoms outside a large cylinder and inside a small cylinder are removed to obtain the faceted nanotubes with different outer and inner diameters, and the nanostructure surfaces are not passivated. All the 1D nanostructures are placed in a tetragonal supercell, and periodic boundary conditions are applied along the axis direction to simulate the infinitely long nanowires/tubes.

DFT-based ultrasoft pseudopotential²⁸ plane-wave method implemented in the Vienna *ab initio* simulation package (VASP)²⁹ was adopted for all the computations. The generalized gradient approximation (GGA) with PW91 functional,³⁰ and a 360 eV cutoff for the plane-wave basis sets were used. For all the systems studied, the coordinates of all the atoms within the supercell were fully relaxed without symmetry constraint during geometry optimizations; the lattice constant *c* was also optimized to minimize the total energy along the tube/wire axis. Five Monkhorst–Pack special *k* points were used for sampling the 1D Brillouin zone, and the convergence threshold was set as 10^{−4} eV in energy and 10^{−3} eV/Å in force.

III. RESULTS AND DISCUSSION

A. Carbon and BN nanostructures

For C and BN nanostructures, it is interesting to find that the faceted nanotubes F1 and F2 both quit their initial configurations and become double-walled nanotubes after the optimization (Fig. 1). F1 consists of an outer zigzag (15,0) SWNT and an inner (9,0) SWNT, while F2 consists of an outer zigzag (21,0) SWNT and an inner (15,0) SWNT. Similar results have been reported by Pan and Feng³¹ in a recent paper. In contrast, the nanowires NW1, NW2, NW3, and the faceted nanotube F3 still keep their initial bulk configuration, though significant reconstruction happens to the surfaces. Especially, the (12,0) single-walled C and BN nanotubes are more stable than all the other C and BN nanostructures considered except the 2D layer (Table I), and F1 and F2 are more stable than F3 after changing into cylindrical forms. The above results are not difficult to understand, since it is well known that C, B, and N atoms all prefer *sp*² hybridized multiple bonds,³² and layered graphite and *h*-BN are their stable phases for bulk materials, respectively. Thus, cylindrical forms of BN and C nanostructures, where C, B, and N atoms all adopt *sp*² hybridization, are energetically more favorable than those C and BN nanostructures in wurtzite configuration with *sp*³ hybridization.

B. AlN, GaN, ZnO, ZnS, and Si nanostructures

The evolution rules of AlN, GaN, ZnO, ZnS, and Si nanostructures are quite similar, but significantly different from C and BN (Table I). The NW3 nanowires always have the largest binding energies, followed by the NW2 nanowires and F3 faceted nanotubes. The binding energies of (12,0) SWNTs of these wurtzite materials are even lower than those of the thinnest NW1 nanowires and the thinnest F1 faceted nanotubes. Since the binding energies of SWNTs increase with increasing tube diameters due to the smaller strain energies, 2D single layer can be seen as a limit of SWNTs with

TABLE I. Binding energies per atom (eV)^a of all nanostructures for each wurtzite material.

	NW1	NW2	NW3	F1	F2	F3	(12,0)	Single layer
C	8.609	8.750	8.817	8.966	9.057	8.751	9.100	9.192
BN	8.256	8.355	8.405	8.510	8.574	8.354	8.613	8.865
SiC	6.848	7.026	7.117	6.862	6.865	7.028	6.871	6.920
AlN	6.694	6.846	6.924	6.705	6.707	6.846	6.651	6.679
GaN	5.775	5.905	5.972	5.783	5.785	5.904	5.745	5.774
ZnO	3.593	3.662	3.698	3.599	3.599	3.662	3.564	3.585
ZnS	3.150	3.191	3.211	3.145	3.141	3.187	3.032	3.058
Si	4.800	4.960	5.040	4.815	4.815	4.965	4.595	4.627

^aThe binding energy per atom is computed with respect to dissociation into atoms, and also as exemplified by BN, $E_b = (nE_B + mE_N - E_{B_nN_m}) / (n+m)$, where n and m are the number of B and N atoms, respectively. E_B and E_N are the energy of B and N atoms, respectively.

an infinitely large diameter and the highest stability. Thus, we computed the single-layered structures of these five materials to estimate the binding energies of infinitely large SWNTs. Our computations show that such single layers have even lower binding energies than those of NW1 and F1. The above results demonstrate that SWNTs of AlN, GaN, ZnO, ZnS, and Si can never be more stable than the faceted ones, even with very large diameters. Although previous studies^{11–14} showed that the strain energies for these tubes are comparable or lower than those of BN and carbon nanotubes, they are only metastable since the faceted tubes are more stable. The SWNT form may be only hypothetical for the above wurtzite materials.

The instability of Si and ZnS SWNTs can be easily understood since Si, Zn, and S are reluctant to adopt sp^2 hybridization.³² However, AlN, GaN, and ZnO all contain a first-row element, which prefers to form sp^2 -hybridized multiple bonds; what is the reason for the instability of their SWNTs compared with BN? It is mainly due to the significant difference in the atomic radius and electronegativity of the elements in these wurtzite compounds (Table II). Due to the large atomic radius difference, the orbital overlap in the SWNTs of these wurtzite compounds is quite small, resulting in much weaker π bonding and less stability. Also the significant difference of electronegativity gives more ionic component to Al–N, Ga–N, and Zn–O bonds which would therefore diminish the conjugated effect of π bonding. In contrast, the atomic radius difference between B and N is relatively small, and the sufficient overlapping of p_z orbits between B and N brings strong delocalized π system and makes BN SWNTs rather stable.

C. SiC nanostructures

In contrast to the above both catalogs of wurtzite materials, the binding energy of (12,0) SiC SWNT is higher than those of F1 and F2, but lower than those of NW2, NW3, and

F3 (Fig. 2). This result is amazing since in the previous studies of wurtzite nanostructures,^{11,21–24} SWNTs are always less stable than faceted nanotubes. Very recently, Wang *et al.*³⁵ have systematically studied the energetics of single-crystalline 2H-SiC nanowires and nanotubes through first principles computations. They claimed that faceted SiC nanotubes are all energetically more favorable than the cylindrical ones. However, the chosen single-walled SiC nanotubes in their study are rather thin. To get more insight, we compared the binding energies of 2D SiC single layer and SiC nanowires and faceted nanotubes, since the SiC single layer can model the infinitely large SiC SWNT with the highest stability. Like (12,0) nanotube, the computed binding energy of SiC single layer is also higher than those of NW1, F1, and F2, and lower than those of NW2, NW3, and F3. It implies that SiC SWNTs can never be more stable than NW2, NW3, and F3. However, since SiC SWNTs are more favorable than thinner faceted nanotubes and nanowires energetically, it gives a reasonable explanation why cylindrical form has been realized experimentally for SiC.

It is the relatively strong preference of the sp^2 -hybridization and moderate differences in atomic radius and electronegativity between Si and C that make SiC SWNTs rather competitive in SiC nanostructures. The atoms in SiC SWNTs are all sp^2 -hybridized, and the p_z orbitals of C and Si are sufficiently overlapped and will form strong conjugated π bonding on the surface of slab and nanotubes, which could lower the total energies. Therefore, graphitic SiC and SiC SWNTs are more stable than those thinner nanowires and faceted nanotubes. However, as the diameter and thickness increase, the ratio of surface saturated atoms versus total ones in nanowires and faceted nanotubes decreases gradually, and then nanowires and faceted nanotubes will be eventually more stable than SWNTs, since wurtzite SiC is the more stable phase than layered structure (which does not exist actually) for bulk material. In comparison, the

TABLE II. Atomic radius (angstrom) (Ref. 33) and electronegativities (using the Pauling scale) (Ref. 34) of elements contented in the studied wurtzite materials.

	C	B/N	Si/C	Al/N	GaN	Zn/O	Zn/S	Si
Atomic radius	0.67	0.87/0.56	1.11/0.67	1.18/0.56	1.36/0.56	1.42/0.48	1.42/0.88	1.11
Electronegative	2.55	2.04/3.04	1.90/2.55	1.61/3.04	1.81/3.04	1.65/3.44	1.65/2.58	1.90

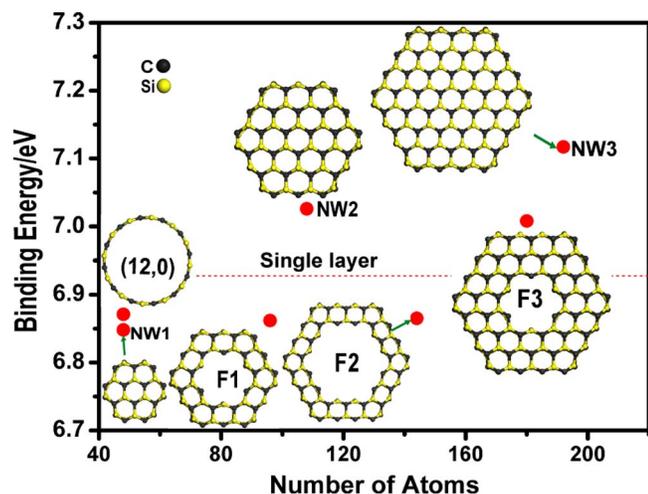
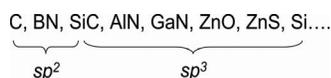


FIG. 2. (Color online) Variation in binding energies with number of atoms for various 1D SiC nanostructures. The dot line denotes the binding energy of 2D SiC single layer.

thinner nanowires and faceted nanotubes of SiC have high ratio of unsaturated surface atoms which leave unfavorable dangling bonds on the surface and thus increase the total energies. Overall, the above results can vigorously explain why SiC SWNTs can be a stable phase in experiments, and account for their high stability even superior to some thin faceted nanotubes. SiC is the transition of nanostructures from sp^2 -dominated to sp^3 -dominated for wurtzite crystals.



IV. CONCLUSION

In summary, the evolution rule of nanostructures for a series of wurtzite materials have been systematically studied using first principles computations. The evolution of wurtzite nanostructures is highly related to their compositions. For C and BN, the single-walled cylindrical forms are energetically more favorable than faceted nanotubes and nanowires since C, B, and N all prefer to adopt sp^2 hybridization. In contrast, the more preferable hybridization for Si, Zn, and S is sp^3 ; therefore, the Si and ZnS SWNTs are much less stable than the faceted nanotubes and nanowires. For AlN, GaN, and ZnO, the nanostructures of these materials are dominated with fourfold-coordination, since the single-walled forms are rather unstable due to the significant difference of atomic radius and electronegativity between two elements involved, which would lower the orbital overlapping and the conjugated effect of delocalized π bonding. Overall, we answer why SiC can form the single-walled tubular structure, while other wurtzite materials, Si, AlN, GaN, ZnO, and ZnS, always form the faceted ones. We hope that our study can bring a deeper understanding of wurtzite nanostructures.

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