

# Origin of the phase transition of AlN, GaN, and ZnO nanowires

Yelong Wu,<sup>1</sup> Guangde Chen,<sup>1</sup> Honggang Ye,<sup>1</sup> Youzhang Zhu,<sup>1</sup> and Su-Huai Wei<sup>2,a)</sup>

<sup>1</sup>Non-Equilibrium Condensed Matter and Quantum Engineering Laboratory, The Key Laboratory of Ministry of Education, School of Science, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

<sup>2</sup>National Renewable Energy Laboratory, Golden, Colorado 80401, USA

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The stabilities of AlN, GaN, and ZnO nanowires/nanorods with different structures and sizes are investigated using first-principles calculations. We found a structure transformation from the graphitelike phase to wurtzite phase as the diameter and length of the nanowire increases. We show that this is due to the competition between the bond energy, the Coulomb energy, and the energy originating from the dipole field of the wurtzite structure. A mechanism of growing uniform nanowires using a graphitelike structure as a precursor is proposed through analyzing the phase diagram of these materials. © 2009 American Institute of Physics. [DOI: 10.1063/1.3159816]

Wide band-gap wurtzite semiconductors such as AlN, GaN, and ZnO have attracted much attention over the past decade because of their superb performance in electronics and optoelectronic applications.<sup>1,2</sup> Forming nanostructures of these materials, especially the nanowires, provides further opportunities of using these materials to design optoelectronic devices.<sup>3-5</sup> This is due to the quantum confinement effects their material properties can be tuned by size as well as shape. For a long time, significant efforts have been devoted to fabricating high-quality nanowires by employing different techniques.<sup>6-8</sup> Although the number of various kinds of nanowires fabricated via different techniques increases dramatically every year, a deeper analysis of the basic process of nanowires formation is still lacking and controlling the growth of the nanowires is still a challenging issue.

In this paper, using first-principles methods, we investigate the formation of nanowires/nanorods of AlN, GaN, and ZnO by calculating their formation energies as a function of size. For these systems, we observe an interesting transformation from graphitelike hexagonal structure (space group  $P6_3/mmc$ , denoted as GL) to wurtzite structure (space group  $P6_3mc$ , denoted as WZ) as the size of the nanowires/nanorods increases. Furthermore, after studying the relative stabilities of the nanowires/nanorods with different diameters, length, and structural phases, and analyzing the variation of electron distributions and the dipoles of the nanorods, we explain the origin of the phase transition and propose an approach of growing uniform wurtzite semiconductor nanowires.

In this work, all the structural optimizations and energy calculations are performed using the density-functional theory in the generalized-gradient approximation.<sup>9</sup> The projected augmented wave method<sup>10</sup> as implemented in the VASP (Refs. 11 and 12) is employed to investigate the nanowires/nanorods. All the nanowires/nanorods are initially constructed from the bulk wurtzite crystal structure with theoretically optimized lattice parameters. The direction of the nanowires/nanorods is chosen to be along the [0001] with the (10 $\bar{1}0$ ) lateral facets.<sup>13</sup> The energy cutoff is set at 500 eV and the atomic structure is relaxed until the force acting on each

atom is less than 0.03 eV/Å. Highly converged  $\mathbf{k}$  points are used for the Brillouin zone integration.

We first calculate the nanowire formation energies using supercells with periodic boundary conditions. The supercell has a square shape in the  $(x,y)$  plane. A vacuum region of about 10 Å is set to decouple the interaction between adjacent nanowires. The supercell length along wire axis  $z$  is equal to  $c$  (lattice parameter). For each structure, the equilibrium lattice size,  $c_{eq}$ , are obtained by minimizing the total energy. Our aim here is to investigate the energetic stability of different phase and how it evolves with diameters. In Fig. 1, we plotted the formation energies<sup>13</sup> of AlN nanowires in the GL and WZ phases as a function of  $c$ . There is a minima corresponding to the optimum structure in each energy curve of different structures. The formation energy of the GL13A (GL phase, 13 atoms per Al-N layer) is 1.097 eV/pair (i.e., per Al-N pair), which is 0.285 eV/pair lower than the WZ13A. It indicates that for this small AlN nanowire, the GL phase is energetically favored than the WZ phase. When the diameter increases, the energy difference becomes smaller. The difference between the GL16A and WZ16A is 0.205 eV/pair and is only 0.083 eV/pair for the GL24A and

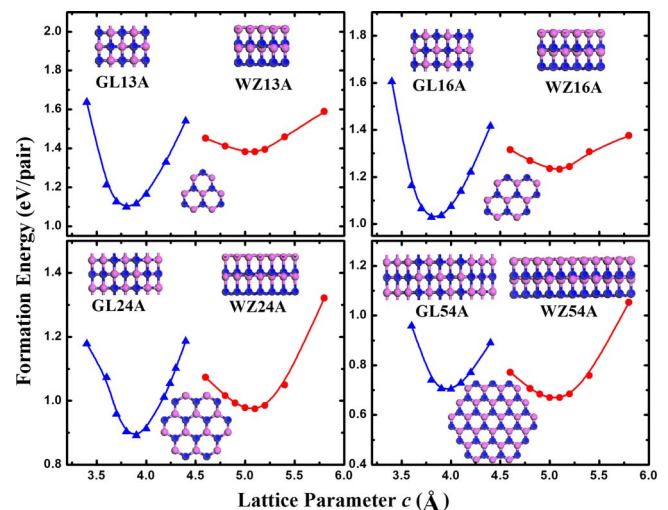


FIG. 1. (Color online) Formation energies of GL and WZ phases of AlN nanowires as a function of  $c$ . The insets are the side and top views of the nanowires.

<sup>a)</sup>Electronic mail: suhuai.wei@nrel.gov.

TABLE I. The number of atoms per supercell  $N$ , optimized supercell length in  $[0001]$  direction  $L$  ( $\text{\AA}$ ), diameter  $D$  ( $\text{\AA}$ ), and the calculated formation energy  $E_f$  (eV/pair) of the GaN nanowires.

Nanowires	$N$	$L$	$D$	$E_f$
GL6A	12	3.90	3.829	1.510
WZ6A	12	5.20	3.713	1.680
GL13A	26	4.10	7.658	1.303
WZ13A	26	5.30	7.426	1.120
GL16A	32	4.10	9.573	1.248
WZ16A	32	5.30	9.283	0.989
GL24A	48	4.20	10.131	1.137
WZ24A	48	5.30	9.824	0.773

WZ24A. That is, the GL phase nanowires are more stable than the WZ phase ones only for small diameter nanowires. For larger diameter ones, the GL phase structures become more and more unstable. When the diameter increases large enough, such as the nanowire with 54 atoms per Al-N layer (denoted as 54A), the WZ phase is more favored as the formation energy for GL54A is 0.034 eV/pair *higher* than for WZ54A. Similar calculations are also carried out for GaN nanowires. In Table I, we listed the structural parameters and formation energies of the GaN nanowires, which suggest that 6A GaN nanowire favors the GL phase while 13A, 16A, and 24A favor the WZ phase. Additionally, Wang *et al.*<sup>14</sup> recently reported a study on ultrathin ZnO nanowires that 13A nanowire choose the GL phase while WZ phase is more stable for 16A, 24A and 54 A. This is consistent with our results of ZnO and similar to what we found in AlN and GaN above.

The results above indicate that as a general trend, there is a structure transformation from GL to WZ as the nanowire diameter increases. To understand the origin of this phase transformation, we analyze the structural and electronic properties of these nanowires. As shown in Table I, a noticeable difference between WZ and GL nanowires is the volume difference between the two phases, which is proportional to  $LD^2$ . Additionally, despite the resemblance in geometric structure, bulk WZ structure has a lower coordination number (4) than GL (5). Therefore, the GL structure has larger (more negative) Coulomb binding energy than the WZ phase. On the other hand, the WZ structure has stronger bond energy than the GL phase. The formation of the nanowire lost the bond energy at the surface. Therefore, for thin nanowires with high surface-to-volume ratio, the GL structure becomes more stable due to its large Coulomb interaction energy, whereas for thick nanowires, the WZ structure regain its stability due to more contribution from the bond energy.

Having discussed the structure transformation of infinite length nanowires as the size of diameters increase, we now examine the structure transformation of finite length nanowires, namely, nanorods, as the lengths of them increases. We use the ZnO nanorods with 16 atoms in one ZnO layer, which is a typical representation of the nanorods, as the example. In this case, the shortest nanorod studied contains two ZnO layers, which we denoted as 16A-2L. Longer nanorods are generated by repeating the structures along the  $[0001]$  direction. To isolate the nanorods, vacuum regions of about 10  $\text{\AA}$  are also chosen in the  $c$  direction. The formation energies of GL and WZ phase nanorods as a function of the number of ZnO layers are illustrated in Fig. 2. It is clear from the figure that for these small diameter nanorods with signifi-

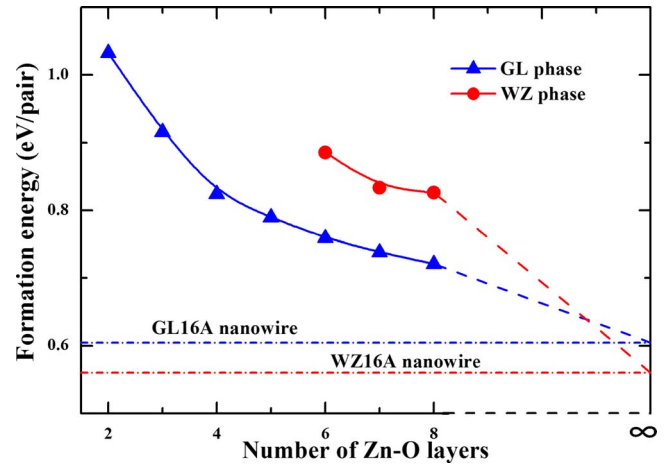


FIG. 2. (Color online) Formation energies of ZnO nanorods as a function of the number of Zn-O layers.

cant surface area, the GL structure is more stable when the nanorods lengths are relatively small, although for nanowire with this diameter, the WZ phase is slightly more stable than the GL phase. For the nanorods WZ16A-2L, WZ16A-3L, WZ16A-4L, and WZ16A-5L, which are initially constructed in WZ phase, they even changed into the GL phase after geometry optimization. The above results suggest that because the WZ16A nanowire is more stable than GL16A, whereas the short GL16A- $n$ L nanorod is more stable than WZ16A- $n$ L, there will be a point of intersection of the two curves in Fig. 2, which means a critical length ( $n_c$ ) at which a phase transition will occur. Similar results are found for all the AlN and GaN nanorods calculated in this study.

To further understand the stabilizing mechanism of the nanorods, we have studied the charge distribution and dipole moments<sup>15</sup> in these nanorods. As one can see in Fig. 3, the charge density distributions on the  $(11\bar{2}0)$  planes of WZ and GL is quite different despite similar covalent bonding character existing between the adjacent Zn-O layers, the centers of positive charge and negative charge do not coincide along the  $[0001]$  direction in the WZ structure, i.e., it has an intrinsic dipole. This dipole generates a macroscopic electrostatic field along the  $c$  axis of nanorod, which also contributes to the destabilization of the WZ phase nanorod. Our calculated result is consistent with this observation. We find that the dipole moments of the GL phase nanorods are close to zero. The calculated dipole moments are 34.5 Debye for the WZ16A-6L and 36.4 Debye for the WZ16A-7L nanorod. By removing the dipole moments using passivating pseudohy-

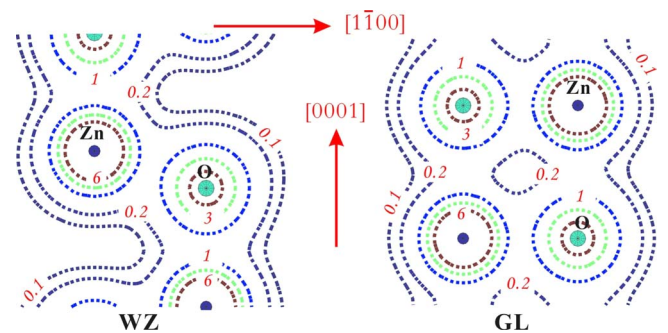


FIG. 3. (Color online) Charge density (in  $e/\text{\AA}^3$ ) on the  $(11\bar{2}0)$  planes of WZ and GL structure.

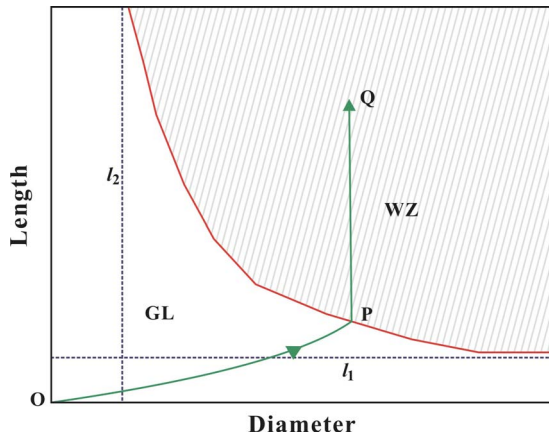


FIG. 4. (Color online) Qualitative phase diagram of AlN, GaN, or ZnO.

drogen, we find that the energy difference between the WZ and the GL nanorods are reduced. Therefore, for the nanorods, it is the competition between the bond energy, the Coulomb energy, and the extra energy originating from the macroscopic electric field of the dipoles that is responsible for the structure transformation.

After establishing the structure transformation mechanism of the AlN, GaN, and ZnO nanowires/nanorods and calculating the formation energy as a function of the diameter and length, we now have sufficient information to plot the phase diagram with respect to the diameters and lengths of the nanowires/nanorods. Figure 4 is a schematic phase diagram of AlN, GaN, or ZnO. The lines  $l_1$  and  $l_2$  are two asymptotes of the coexistence border. Line  $l_1$  corresponds to the transformation length for the infinite large diameter nanorod (film), that is, the transformation thickness for the film.<sup>16,17</sup> Similarly, line  $l_2$  corresponds to the transformation diameter for the infinite length nanowire.

The phase diagram shown in Fig. 4 suggests a possible growth route of a WZ structured nanowire, i.e., path  $O \rightarrow P \rightarrow Q$  in Fig. 4. The process of  $O$  to  $P$  lies in the GL structure region, reflecting the fact that in the early stage of nanowire growth, the GL structure is more favored. As the growth process continues, the diameter of the nanowires grows larger and the length grows longer. Finally, they will reach a threshold values corresponding to the  $P$  point, where the GL and the WZ structure will coexist. After that, the structure transformation occurs and the system is more stable in the WZ structure. Along with the structure transformation, an electric dipole moment associated with the WZ structure will appear. This dipole will generate an electric field around the nanowire and the radicals used in the growth will be attracted toward the place with the strongest field strength, that is, the top surface of the nanowire. Due to a much larger electrostatic attractive forces, the incoming radicals will land on the top surface of the nanorod and are barely able to have a chance to hit the sidewall.<sup>15,18</sup> In this way, the nanowire will grow along the  $[0001]$  direction with the diameter un-

changed. This is described as the path  $P \rightarrow Q$ , which is perpendicular to the horizontal diameter axis. This understanding of the growth process of the nanowires suggests that in order to control the diameter of the nanowire, one must focus on the initial precursor, i.e., the GL structure. If one can control effectively the first stage of growth, so the WZ phase always starts to grow at the point  $P$  of the phase diagram, then uniform nanowires with fixed diameter could be synthesized.

In summary, using first-principles calculations, we have investigated the stability of AlN, GaN and ZnO WZ nanowires/nanorods along  $[0001]$  direction with the  $\{10\bar{1}0\}$  lateral facets. We found a structure transformation from the GL to WZ as the diameter and the length of the nanowire increases. We show that this is due to the competition between the bond energy, the Coulomb energy, and the energy originating from the macroscopic electric field of the dipoles in the WZ structure. Empowered by the understanding of the stability of the nanowires/nanorods with different phases and sizes, we plotted the schematic phase diagram and proposed a growth method to control the diameters of the nanowires/nanorods using the GL structure as precursors. Though all of our discussions in this paper are focused on AlN, GaN, and ZnO nanowires/nanorod, we believe that the general mechanism of the growth discussed here can also be applied to other nanostructures.

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