Structural transformation of ZnO nanostructures

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Many nanostructures experience structural transformation, either from one type of crystalline structure to another or from one orientation to another orientation within the same crystalline structure. Using a combination of *ab initio* calculations and analytical formulation, we show that such structural transformation is a direct result of surface reconstruction. In particular, our *ab initio* results show that infinite large ZnO nanoplates and infinite long ZnO nanowires transform from wurtzite to graphitic structure below a critical thickness or diameter. Our analytical formulation further shows that nanowires of finite length can go through the same structural transformation at larger critical diameters.

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Surface reconstruction (including pattern formation and relaxation) is common among crystalline materials, more so for covalent materials than for metals. For example, various reconstructions such as 7x7 on Si{111} surfaces have been documented.[1-3] The surface reconstruction forces atoms to reorganize on surface so as to enhance bonding. A thin gold foil of {100} surfaces spontaneously transform into another orientation with {111} surfaces.[4] With even larger surface to volume ratios, copper nanowires go through similar transformations.[5, 6]

Zinc oxide (ZnO), which exists in wurtzite and rocksalt structures,[7] transforms into graphitic structure when it is in the form of thin nanoplates.[8, 9] Uniaxial strain of ZnO nanowires along $[01\bar{1}0]$ can also lead to such transformation.[10] Looking at the fundamental physics, one sees the generic link of these transformations. Once a free surface exists, atoms on the surfaces have missing bonds and therefore tend to reorganize to maximize bonding. This tendency leads to surface reconstruction and imposes a strain (or stress) on the atomic layers below. The surface reconstruction may favor a particular crystalline structure or a particular surface orientation of a crystalline structure, and the imposed strain has similar effects. Based on this generic scenario, transformation to graphitic structures should be general among ZnO nanostructures, instead of unique feature of ZnO nanoplates only.

Using *ab initio* calculations and analytical formulation, we establish the general transformation behavior of ZnO nanostructures. In the following, we first briefly describe the *ab initio* calculation methods, and continue with *ab initio* results of relative structural stability of ZnO bulk, infinite large ZnO nanoplates, and infinite long ZnO nanowires. Based on the *ab initio* calculation results, we formulate the critical condition when ZnO nanowires of finite lengths and finite diameters are stable in graphitic structure.

The *ab initio* calculations, within the framework of density functional theory, are based on the VASP code.[11] We use the generalized gradient approximation (GGA) of Perdew and Wang [12] to represent the exchange correlation and the projector augmented wave (PAW) method [13]; and choose the cutoff energy in wave expansion to be 500 eV and the k-point mesh for Brillouin integration to be 4x4x4. In the thin film calculations, the simulation slab is made up of a vacuum region of at least 10 Å and the ZnO double layers. In the nanowire calculations, the slab includes a ZnO core and a surrounding vacuum region with a total thickness in any direction being of at least 10 Å as well.

In order to understand the bonding nature, our *ab initio* calculations start with the binding energy of bulk crystals. As shown in Fig. 1, although the energy of graphitic ZnO is always higher than that of wurtzite, the graphitic structure may exist as a metastable structure.[14] More importantly,

Fig. 1a shows that in the graphitic structure, each Zn (or O) has a five near neighbors, three in-plane neighbors of 0.20 nm away and two out-of-plane neighbors of 0.23 nm away. The in-plane bonds are stronger, as indicated by higher electron density, than the out-of-plane bonds. In contrast, each Zn (or O) has four near neighbors of 0.20 nm away in the wurtzite structure, and six near neighbors of about 0.22 nm away in the rocksalt structure.

Instead of searching for a route to realizing the metastable graphitic ZnO structure, we focus on the stabilization of such structure at the nanoscale. Previous *ab initio* calculations have shown that below a critical thickness of nine double layers, the $(0001)/(000\bar{1})$ nanoplate of infinite large diameter transforms from wurtzite to graphic structure. Our calculations have confirmed that this conclusion is unaffected when the computational cell goes from 1x1 to 2x2 to 3x3 to 4x4 along the surface.[9] Two points are worthy mentioning here. One, the bulk graphitic structure is energetically less preferred than bulk wurtzite structure; with a binding energy difference of 0.13 eV per ZnO molecule. Two, a $(0001)/(000\bar{1})$ surface atom will only lose one of five bonds in the graphitic structure, but one of four bonds in the wurtzite structure. Further, on the $(0001)/(000\bar{1})$ surface, the lost bond in the graphitic structure is the weaker bond of the five. These two points suggest that it is the surface reconstruction that drives the transformation of the nanoplate from wurtzite to graphitic structure. As a further evidence of the importance of surface reconstruction (and relaxation), both bond angle and inter-atomic layer spacing change substantially. On a $(0001)/(000\bar{1})$ surface of thick plate, the original tetrahedral bond angle goes from 109° to 117° (closer to 120° in graphitic structure). At the same time, the spacing of nearby Zn and O layers goes from 0.066 nm to 0.005 nm (closer to 0 nm in graphitic structure). Such changes propagate into the four double layers from surface, with decreasing magnitude.

Following the logic of surface reconstruction being the driving force, we next consider nanowires along the [0001] direction. Three nanowires of infinite length (represented through the periodic boundary condition) and various diameters are shown as the inset of Fig. 2. For smaller nanowires (NW #1 and NW #2), the graphitic structure, as indicated by the smaller *c/a*, is energetically more preferred than the wurtzite structure. As the diameter increases (NW #3), the graphitic structure becomes energetically less preferred than the wurtzite structure. According to these results, [0001] nanowires of infinite length undergo a transformation from wurtzite to graphitic structure below the critical diameter of 1.3nm – the diameter of NW #2. Once again, each surface atom loses one of five bonds in graphitic structure, in contrast to one of four bonds in wurtzite

structure. Going from wurtzite to graphitic structure, the energy decrease on surfaces can compensate the energy increase in the core of the nanowire. Therefore, it is also the surface reconstruction that drives the transformation of nanowires from wurtzite to graphitic structure.

Having established the structure transformation of nanoplates of infinite large diameters and nanowires of infinite length, we now examine nanostructures of finite dimensions in both directions – [0001] nanowires of finite length and finite diameter. Consider a nanowire, schematically shown as the inset of Fig. 3. In forming the nanowire, n_1 pairs of out-of-plane bonds are missing, and n_2 pairs of in-plane bonds are missing (cf. Fig. 1a); since Zn and O bonds differ, we consider the bonds in pairs: the bond to Zn and that to O. For each pair of out-of-plane missing bonds, the energy increase in graphitic structure is different by ΔE_1 from wurtzite structure ($\Delta E_1 < 0$). Similarly, for each pair of in-plane missing bonds, the energy increase in graphitic structure is different by ΔE_2 from wurtzite structure ($\Delta E_2 < 0$ as well). At the same time, the binding energy of each ZnO pair is 0.13 eV higher in bulk graphitic than in wurtzite. For a total of N ZnO molecules in a nanowire, the energy difference between graphitic structure and wurtzite structure is:

$$\Delta E = n_1 \cdot \Delta E_1 + n_2 \cdot \Delta E_2 + N \cdot 0.13 \qquad (1)$$

Using unrelaxed wurtzite structure as the reference, we can relate the n_1, n_2, and N to the length L and diameter D of the nanowire by: $n_1 = \dfrac{\pi}{2\sqrt{3}}(\dfrac{D}{a})^2$, $n_2 = \pi(\dfrac{L}{c})(\dfrac{D}{a})$, and $N = \dfrac{\pi}{\sqrt{3}}(\dfrac{L}{c})(\dfrac{D}{a})^2$, where a and c are the lattice constants as shown in Fig.1a. In terms of the nanowire diameter D and length L, the energy difference becomes:

$$\Delta E = \frac{\pi}{2\sqrt{3}}(\frac{D}{a})^2 \cdot \Delta E_1 + \pi \cdot (\frac{L}{c})(\frac{D}{a}) \cdot \Delta E_2 + \frac{\pi}{\sqrt{3}}(\frac{L}{c})(\frac{D}{a})^2 \cdot 0.13 \qquad (2)$$

The critical condition for graphitic-wurtzite structure transformation is defined as $\Delta E = 0$. Using the *ab initio* results of nanoplate and nanowire, we fit the surface energy differences ΔE_1 and ΔE_2. For the nanoplate of infinite large diameter, the critical dimensions are $L/c = 9/2$ and $D/a \to \infty$; and therefore $\Delta E_1 = -1.17 eV$. For the nanowire of infinite length, the critical dimensions are $L/c \to \infty$ and $D/a = 4$; and therefore $\Delta E_2 = -0.30 eV$. Now, the critical condition $\Delta E = 0$ becomes:

$$-1.06 \cdot (\frac{D}{a})^2 - 0.943 \cdot (\frac{L}{c})(\frac{D}{a}) + 0.236 \cdot (\frac{L}{c})(\frac{D}{a})^2 = 0 \qquad (3)$$

Shown in Fig. 3, the separatrix given by equation (3) separates the domains of stable wurtzite and graphitic structures.

Before closing, we note that we have left out the rocksalt structure in the analyses. At ambient

temperature and pressure, wurtzite is the stable structure, and the stability of rocksalt structure requires large pressure. Even with surface stress, such high pressure is unlikely reached. Therefore, the transformation of wurtzite to rocksalt structure is much less likely than that of wurtzite to graphitic structure. We also like to point out that the change of crystalline structures is accompanied by change of electronic structures. The bulk graphitic structure has a band gap larger than that of bulk wurtzite structure by 0.3 eV, and the gap is even larger for nanoplates; for nanoplate of seven double layers, there is an extra 0.1 eV on top of the 0.3 eV. In contrast to metallic nature of wurtzite nanoplates, graphitic nanoplates are semiconducting.

In summary, this work shows that surface reconstruction leads to structure transformation of nanostructures, including the ZnO nanostructures reported in this Letter and others reported elsewhere. Our *ab initio* calculations determine the critical dimensions of wurtzite-graphitic structure transformation for nanoplates of infinite diameter and nanowires of infinite length. Based on these *ab initio* calculations, our analytical formulation has led to a phase diagram of wurtzite and graphitic structural stability.

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Figure Captions

FIG. 1   (Color online) (a) Three crystalline structures of ZnO, and electron distribution in the graphitic structure;

and (b) Binding energy vs atomic molecular volume, all normalized with respect to wurtzite ZnO. In (a) larger

balls represent Zn and smaller balls O, and symbols a (a') and c (c') are in-plane and out-of-plane lattice constants.

FIG. 2   (Color online) Energy (normalized with respect to that of bulk wurtzite ZnO) vs c/a ratio for three

infinite long [0001] nanowires; the bulk case is included for comparison.

FIG. 3   (Color online) Phase diagram of graphitic and wurtzite ZnO nanostructures.

(a)

Wurtzite

Rocksalt

Graphitic

In-plane bond

Out-of-plane bond

(b)

- Wurtzite
- Graphitic
- Rocksalt

Energy per ZnO Molecule(eV)

Normalized Volume