

Research Article

First-Principles Studies on the Structural Transition of ZnO Nanowires at High Pressure

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The structural transition of ZnO nanowires at high pressures from wurtzite to rocksalt structure has been studied by first-principles density functional calculations using the SIESTA code. The size effect was studied by calculating a series of nanowires with different diameters, and the doping effect was studied by ion substitution. It is found that the critical pressure of structural transition for nanowires is lower than that of the bulk, and it decreases as the diameter of the nanowire decreases. It is also found that Mn doping can reduce the transition pressure. The size effect and doping effect are discussed in terms of the chemical bonding and energies of the nanowires.

1. Introduction

It is well known that zinc oxide is a wide band gap ($E_g = 3.37$ eV) semiconductor with interesting electronic, piezoelectric, and photoconducting properties. It has a wide range of applications in electronics, optoelectronics, photovoltaic, and sensors [1, 2]. One of the research highlights is the structural transition from the wurtzite (B4) structure (space group P63mc) to the rocksalt (B1) structure (space group FM $\bar{3}$ M) at high pressure. Experimentally, in situ observations were performed, such as energy dispersive X-ray diffraction [3–5], Raman scattering [6], and X-ray-absorption near-edge structure (EXAFS) [7]. At the same time, theoretical efforts were also made by first-principle calculation using various methods, such as the early Hartree-Fock method [8], LDA and GGA [9], and SIC [10]. Recently, the transition path has also been studied [11–13]. Experimental investigations on the phase transformation of ZnO nano-materials have appeared recently, such as ZnO nano-particles [14, 15], nanorods [16], nanotubes [17], and nanocrystalline [18]. Theoretical works on the structural transition have appeared recently, such as the phase transformation in ZnO nanowires under tensile load [19, 20] and the critical dimension for phase transition of nanowires [21]. However, experimental results about the structure transition are scattered in a wide range, and far

from conclusive. Theoretical studies on the pressure-induced phase transitions in ZnO nanomaterials are in the early stage and further studies are needed.

In this work, the pressure-induced-phase transitions in ZnO nanowires were investigated by first-principles calculations, and the size effect and doping effect were investigated.

2. Theoretical Details

First-principles calculations were performed using the SIESTA package [22, 23] employing pseudopotential and numeric atomic orbits basis. In the calculation, GGA-PBE type of exchange correlation functionals and DZP basis set were used. The mesh cutoff was 400 Ry and Kgrid_cutoff 25 Å. The transition pressure is evaluated by calculating the ground state energy versus cell volume ($E\sim V$) curves. First, the ground state energy of the fully relaxed unit cell is calculated. Then, a series of ground state energies are calculated for unit cells scaled by a set of scale factors. The parameters regarding the structural transition were obtained from the common tangent of the $E\sim V$ curves of the two phases, since the enthalpy $H = U + PV$ is minimum for stable phases in constant pressure systems. The structural transitions of the bulks are calculated first to serve as a basis for further comparison. In order to calculate nanowires, the supercell used in the calculation is a rectangle box

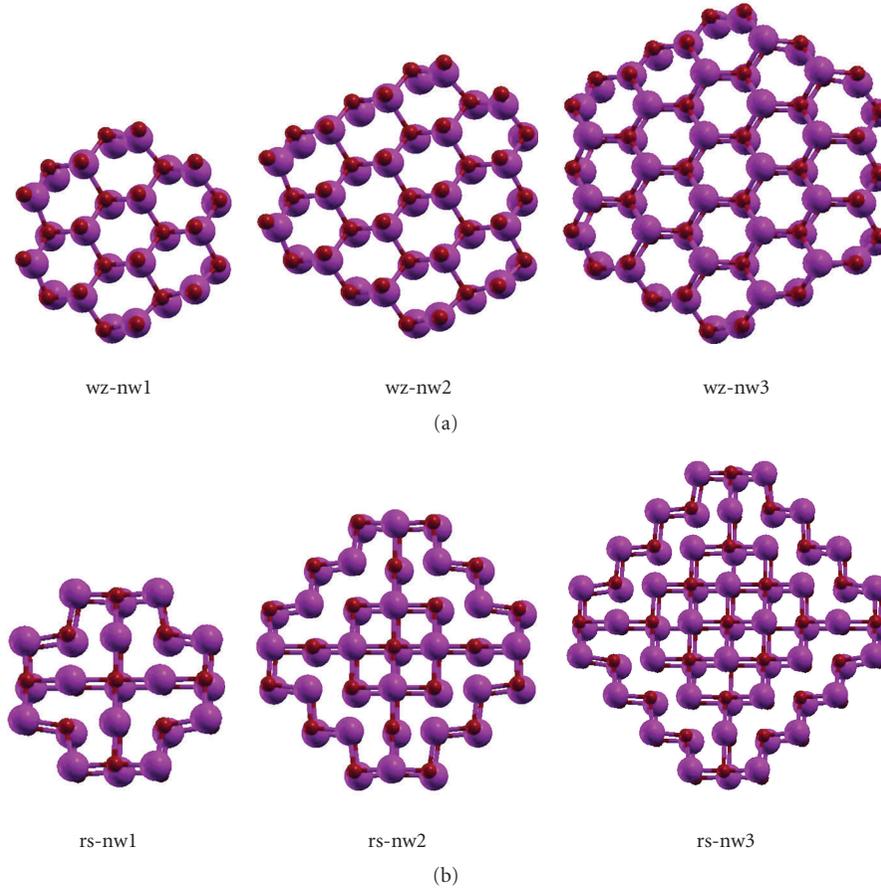


FIGURE 1: The cross-section views of the ZnO nanowires, (a) wurtzite, (b) rocksalt structures. The diameter increases from left to right and the names of the nanowires are shown.

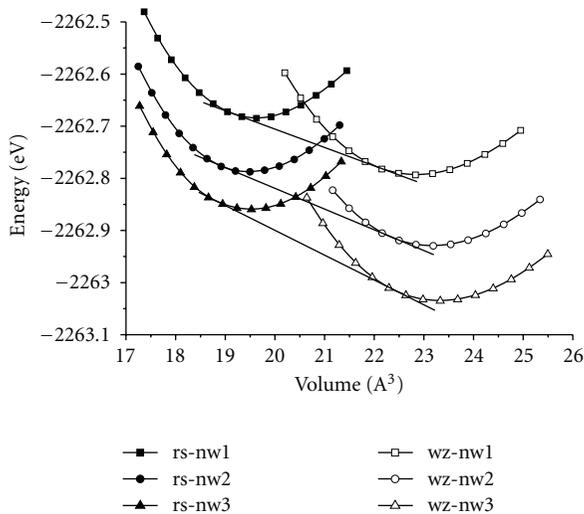


FIGURE 2: The calculated $E\sim V$ curves of three pairs of ZnO nanowires.

with a nanowire in the center. The separations between the nanowires are larger than 10 \AA to eliminate the interactions between the adjacent nanowires. The cross-sections of the nanowires are shown in Figure 1.

3. Results and Discussion

3.1. Pure ZnO Nanowires with Different Diameters. The calculated $E\sim V$ curves of the three pairs of nanowires are plotted in Figure 2. To facilitate comparison, the energy and volume are for each ZnO formula unit. We can see that as the diameter of the nanowires decreases, the ground state energy per ZnO unit increases. This is understandable because the amount of surface atoms and broken bonds increases as the diameter decreases. The equilibrium volume of rs-ZnO nanowires is lower than that of wz-ZnO nanowires, as in the case of bulks. Common tangents are drawn for all the three pairs of $E\sim V$ curves, and the E and V values at each tangent points, where structural transition occurs, were obtained and listed in Table 1.

From the obtained energy and volume data at the points of structural transition, the volume change ($\Delta V/V_0$) and transition pressure (P_{tr}) can be calculated. For comparison, the structure transition of bulk ZnO was calculated using exactly the same calculation parameters, and all the results are listed in Table 1. It can be seen clearly that both the volume change and the transition pressure of ZnO nanowires are lower than that of the bulk and decrease as the diameter of the nanowires decreases. Comparing the experimental transition pressure of 13~14 and 10.5 GPa for

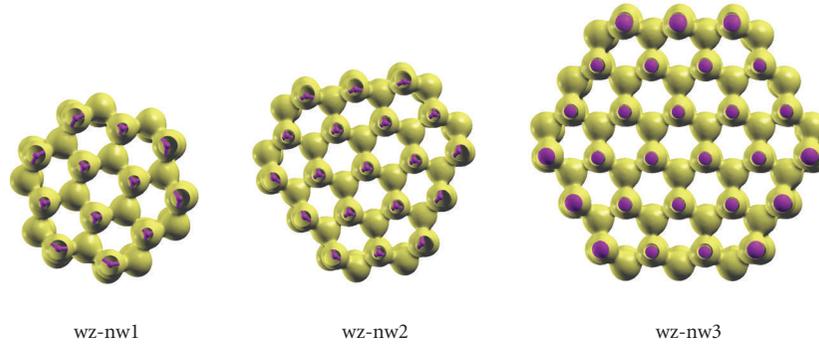


FIGURE 3: The isosurface at $0.06/\text{\AA}^2$ of wz-ZnO nanowires with different diameters.

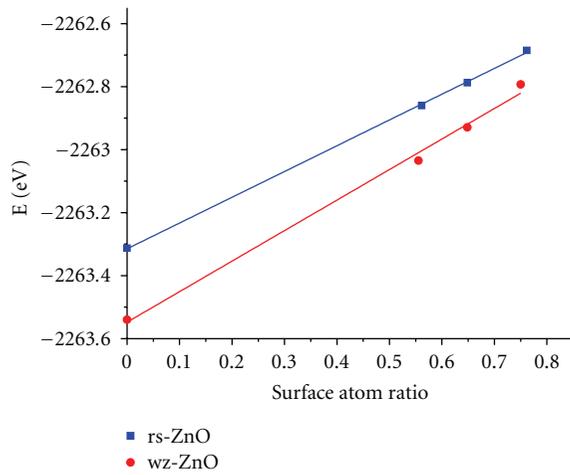


FIGURE 4: The ground state energy per ZnO formula unit as functions of surface atom ratio for wurtzite and rocksalt ZnO nanowires.

nanocrystalline [14, 18], 8.0 GPa for nanorods [16], 11.0 GPa for nanotube [17], and the theoretical results of 8.2 GPa for nanowires by molecular dynamics [20], our results are reasonable.

In order to understand the physical origin of the change in transition pressures, the structure of the nanowires and its change with diameter were investigated. From Figure 1, it can be seen that after geometry relaxation, the positions of the atoms are moved to form compact surface layers. To get a more clear view of the picture, the electron density isosurfaces for the three wz-ZnO nanowires at $0.06/\text{\AA}^3$ are shown in Figure 3. It can be seen that connections between the surface atoms are stronger than those of the inner atoms, as indicated by the larger open connection circles and thicker necks between the atoms. Strong surface bonds and weak core bonds are presented in the ZnO nanowires.

Recently, Ding and Wang observed reconstructed ZnO surfaces [24], and Zhang and Huang claimed that surface reconstruction can affect structural transition [21]. In order to get a clear picture on how the surface layers contribute to the change of transition pressure, the crystal structure and bonding in the nanowires were investigated. The lattice

constants along the c axis are 5.350, 5.331, 5.320 and 5.234 \AA for the three nanowires and the bulk, respectively. It is quite clear that the lattice constant c is larger than that of the bulk and increases as the diameter decreases. Measurement of the lattice constants in the cross-section found that the distances between the core atoms are almost unchanged and those between the surface atoms are shortened. Thus, the chemical bonds between the core atoms are weakened and the extent of the weakness increases as the diameter of the nanowires decreases, which may lead to the observed results.

There is another factor that is directly related to the observed phenomena: the dangling bonds of the surface atoms. The smaller the diameter of the nanowires, the larger the surface to bulk atom ratio, and resulting in more dangling bonds. Figure 4 shows the ground state energies of the ZnO nanowires as functions of surface atomic ratio. It is quite clear that the ground state energy increases almost linearly as the surface atomic ratio increases. Dangling bonds dominate over the close packed reconstructed surfaces in the structure transformation of ZnO nanowires. From the slopes of the two curves, it can be seen clearly that the ground state energy of the wurtzite structure increases much faster than that of the rocksalt structure, and the energy difference decreases which directly leads to the decrease of transition pressure. This can be explained in terms of the bonding characteristics. The coordinate numbers of ZnO in wurtzite and rocksalt structures are 4 and 6, and the surface atoms have 1/4 and 1/6 dangling bonds, respectively. Thus the increase in energy is high for wurtzite structure.

3.2. Mn-Doped ZnO Nanowires. In order to investigate the effect of doping on the structural transformation of ZnO nanowires, first-principles calculations were performed on Mn-doped ZnO nanowires. Doping was realized by substituting a Zn ion with a Mn ion in the supercell. Favorable doping sites were selected by calculating the ground state energies of all the distinct doping sites and searching for the most stable site. Figure 5 shows the relaxed ball-and-stick models of the favorable doping site after geometry relaxation. It can be seen that the favorable dopant sites are near the surface of the nanowires and distortion induced by doping can be seen clearly. In the case of rocksalt ZnO nanowires, distortion due to doping extend to a large area and changes

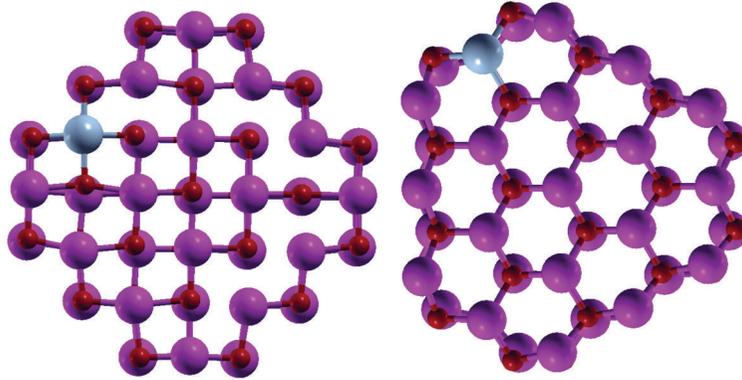


FIGURE 5: The ball-and-stick models of Mn-doped ZnO nanowires after geometrical relaxation.

TABLE 1: The calculated results of structural transition of ZnO nanowires.

Subject	Volume (\AA^3)		$\Delta V/V_0(\%)$	Energy (eV)		P_{tr} (GPa)
	rs-ZnO	wz-ZnO		rs-ZnO	wz-ZnO	
nw1	19.132	22.097	13.4	-2262.675	-2262.779	5.64
nw2	18.933	22.330	15.2	-2262.777	-2262.912	6.35
nw3	18.785	22.369	16.0	-2262.842	-2263.013	7.63
Bulk	18.804	22.736	17.3	-2263.291	-2262.779	8.92

TABLE 2: The calculated results of structural transition for Mn-doped ZnO nanowires.

Sample	Volume (\AA^3)		$\Delta V/V_0$	Energy (eV)		P_{tr} (GPa)
	rs-ZnO	wz-ZnO		rs-ZnO	wz-ZnO	
Bulk	18.804	22.736	0.173	-2263.291	-2263.510	8.92
nw2	18.933	22.330	0.152	-2262.777	-2262.912	6.35
Mn-nw2	19.045	22.480	0.153	-2229.891	-2230.009	5.51

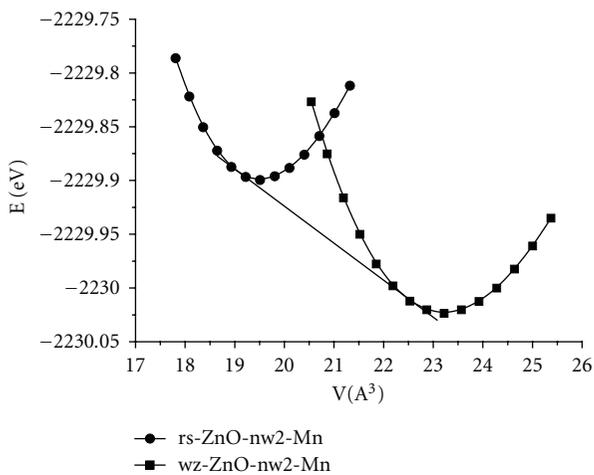


FIGURE 6: The calculated $E \sim V$ curves of the pure and Mn-doped ZnO nanowires.

in bonding can be seen clearly beyond two bonds, while distortion due to doping is restricted in local area for wurtzite ZnO due to their bonding characteristics.

A pair of $E \sim V$ curves were calculated in the same way as in the pure ZnO nanowires and were shown in Figure 6. The results about structural transition are obtained for Mn-doped ZnO nanowires and listed in Table 2, together with the results of the pure nanowires and the bulk for comparison. It can be seen that the critical pressure for structural transition (P_{tr}) of Mn doped ZnO nanowires is lower than that of the pure ones. This is in agreement with experimental results [25].

The decrease of transition pressure in Mn doped ZnO nanowires can be explained in terms of the doping energy affected by bonding characteristics. The elastic energies induced by doping are different for the two structures. Due to the ionic bonds and high coordinate number, strain is extended to a large region in the rocksalt phase, resulting in a moderate strain energy; meanwhile, due to the covalent bonds and low coordinate number, strain is concentrated in a small region for the wurtzite phase, resulting in a high strain energy. Therefore, relative energy of the two phases was reduced and the slope of the common tangent of the two $E \sim V$ curves decreased, which leads to the decrease in transition pressure.

4. Conclusions

Study on the transitions of ZnO nanowires from wurtzite to rocksalt structure at high pressures by first-principles calculations found that the transition pressure of ZnO nanowires is lower than that of the bulk, and it decreases as the diameter of the nanowire decreases. After investigating the structure and chemical bonds of the nanowires, it is found that surface reconstruction leads to close-packed surface layers and sparse core regions. Dangling bonds of the surface atoms lead to the increase of the ground state energy and the large increasing rate of the wurtzite structure caused the decrease of the transition pressure. Mn doping can reduce the critical pressure of structural transition, which is due to the different elastic energies of Mn doping in the two structures.

Acknowledgments

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