

## First-principles study of the wurtzite-to-rocksalt homogeneous transformation in ZnO: A case of a low-transformation barrier

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A homogeneous wurtzite-to-rocksalt phase transformation in ZnO is studied using a first-principles pseudo-potential method. The calculated transformation enthalpy barrier at the phase equilibrium transition pressure is much lower than the barriers previously studied in SiC and GaN. SiC, GaN, and AlN are found experimentally to transform at a pressure significantly higher than their respective phase equilibrium transition pressures. Interestingly we note that the experimentally observed transition pressure in SiC, GaN, and AlN occur for roughly the same value of the enthalpy barrier. In contrast, ZnO readily transforms at the phase equilibrium transition pressure consistent with the fact that its enthalpy barrier at that pressure is well below this critical barrier value.

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Pressure-dependent crystal structures of group-IV, -III-V, and -II-VI materials have been a long-standing topic of interests from both experimentalists and theorists. It is known that, under ambient pressure, the highly covalent materials favor the fourfold coordination structures [zinc blende and/or wurtzite (WZ)], whereas the highly ionic materials favor the sixfold [rocksalt (RS)] and higher coordination structures (for, e.g., CsCl structure). As pressure increased, covalent materials transform into the higher coordination structures. The degree of ionicity is an important factor that determines the transformation pressure. For example, the highly covalent material SiC starts to transform into RS at a pressure of  $\sim 100$  GPa,<sup>1</sup> whereas the less covalent material GaN starts to transform at a much lower pressure of  $\sim 50$  GPa.<sup>2</sup> The higher ionic materials such as MgO and CdO even favor rocksalt phase already at zero pressure (our prior study<sup>3</sup> has shown that if the density of MgO is approximately 17% lower — corresponding to a negative pressure of 16.2 GPa — the hexagonal phase would have been stable). ZnO is a WZ material with a moderate degree of ionicity (increasing the tendency to form in RS structure). Because the cohesive energy of both phases are so close, the WZ-RS transformation pressure in ZnO is rather low [9.1 GPa (Ref. 4)], suitable for performing experiments. On the theory side, phase equilibrium transition pressure can be calculated. Most of the time, this has been done by calculating the energy-volume curves of the two phases and finding the common tangent. In the past, the calculated equilibrium transition pressure is frequently used to compare directly with the observed transformation pressure. It is now realized that there may be large kinetic barriers that impede the transition at the equilibrium pressure, leading to a hysteresis between the forward and backward transformations.<sup>5</sup> The large hysteresis has indeed been observed in the transformations of SiC (Ref. 6) and GaN.<sup>7</sup> This means, in order for the actual transformation process to take place, not only the enthalpy of the ending phase (in this case RS) has to be lower than or equal to the starting phase (in this case WZ) but also the enthalpy barrier of the transformation between the two phases has to be sufficiently low. To meet the later requirement, the observed transformation pres-

sure can be several GPa higher than the equilibrium transition pressure. For examples, GaN and SiC have high observed transformation pressures of  $\sim 50$  and  $\sim 100$  GPa in comparison to the calculated equilibrium transition pressures of 31 GPa (Ref. 8) and 60 GPa,<sup>9</sup> respectively. Interestingly, for ZnO, the observed transformation pressure of 9.1 GPa (Ref. 4) essentially falls in the narrow range of the calculated equilibrium transition pressures, varied between 6.6 GPa (Ref. 10) and 10.45 GPa,<sup>11</sup> indicating that ZnO has a very small transformation barrier.

Since the barrier of transformation has an influence on the transformation pressure, it is challenging to use it to improve the prediction of transformation pressures. We propose that, by monitoring the decrease of enthalpy barrier with pressure and looking for the pressure that gives the threshold barrier (the barrier that is low enough for the transformation to take place), we can obtain a transformation pressure in the cases where the barrier dominates the transformation. A simple homogeneous transformation path between WZ and RS GaN has recently been proposed based on first principles calculations.<sup>8</sup> This path was also shown to be a special case of a more general transformation path between arbitrary tetrahedrally coordinated polytypes of SiC and RS.<sup>9</sup> Furthermore, essentially the same path was actually proposed as early as 1998 in CdS based on shock-wave experimental studies.<sup>12,13</sup> This path has additional experimental confirmation in the studies of phase transitions in nanoparticles of CdSe.<sup>14</sup> While the large volume change in the transition complicates the process of transformation, it is clear that the homogeneous transformation considered here provides a useful description of the nucleation process of the transition and thus its barrier should be a good indicator for when the actual transition can take place.

Our prior homogeneous WZ-RS phase transformation study in GaN (Ref. 3 and 8) and the work of Lambrecht group in SiC (Ref. 9) predict a rather high transformation enthalpy barriers (at the phase equilibrium transition pressure) in these two materials that qualitatively explain the high observed transformation pressures. In this report, using the barriers from those works combining with the additional

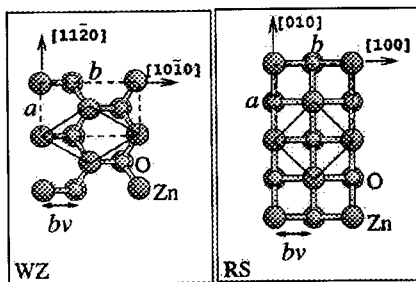


FIG. 1. (Color online) Top views of WZ (left) and RS (right) crystal structures: small spheres, O; large spheres, Zn. The parameters  $b$  and  $v$  defining the structure are indicated.

new results for ZnO and AlN, we will try to quantitatively reconcile the barrier information with the observed transformation pressure.

In addition to the physically unique properties mentioned above that make ZnO a prime candidate for a detailed phase transformation study, there are at least two more reasons to study ZnO. (1) There was a continuing interest in ZnO high-pressure phase transitions since the time it was observed experimentally in the 1960's.<sup>15</sup> These include several experiments and computations.<sup>16</sup> (2) ZnO is a wide-band-gap material with potential applications for blue-optoelectronic devices. For band-gap engineering, alloying with MgO and CdO have been proposed to use to create a wide-gap and narrow-gap ZnO alloy, respectively.<sup>17</sup> Since CdO and MgO both have RS structure, this detailed study of the WZ-RS transformation in ZnO could aid in better understanding the stability of WZ phase in such alloys.

We use the density functional theory, as implemented in the VASP code,<sup>18</sup> with local density approximation (LDA) and ultrasoft pseudopotentials.<sup>19</sup> Zinc 3d electrons were treated as valence electrons. The cutoff energy for the plane wave expansion is 400 eV, the  $k$ -point set is based on a  $7 \times 7 \times 7$  division of the reciprocal unit cell, resulting in approximately 60 inequivalent  $k$  points.

First, we reinvestigated the end phases, i.e., the WZ and RS structures separately. The WZ crystal structure is characterized by three parameters, the lattice constant  $a$ , the  $c/a$  ratio, and the internal parameter  $u$  which fixes the relative position of the two hexagonal close-packed sublattices. The last parameter has to be relaxed for each  $c/a$  when we consider uniaxial strain in the  $c$  direction. To characterize the hexagonal-symmetry-breaking in-plane strain, following Ref. 8, we introduce two additional parameters, the  $b/a$  ratio and the internal parameter  $v$ . The top view of wurtzite crystal (left panel, Fig. 1) is equivalent to the top view of a side-centered orthorhombic structure with the structure parameters  $a$  and  $b$  with  $b/a=1.733$ . The additional internal parameter  $v$  defines the relative in-plane projection of two sublattices. Similar to  $u$ ,  $v$  has to be relaxed for each  $b/a$  when we consider in-plane strain. To be precise, both  $u$  and  $v$  have to be relaxed for each strained structure. The values of all five parameters as well as the volume per pair of WZ- and RS-ZnO are listed in Table I. The RS phase has a smaller volume, by 17.8%, and a slightly higher total energy, by 0.2 eV/pair, in comparison to the WZ phase. Our calculated

TABLE I. Crystal parameters and selected properties of ZnO in WZ and RS structures. The values in square brackets are the parameters at equilibrium phase transition pressure.

	WZ	RS
Volume ( $\text{\AA}^3/\text{pair}$ )	22.8 [21.8]	18.7 [18.0]
$c/a$	1.61 [1.61]	1.00 [1.00]
$u$	0.38 [0.38]	0.50 [0.50]
$b/a$	$\sqrt{3}$ [ $\sqrt{3}$ ]	1.00 [1.00]
$v$	1/3 [1/3]	0.50 [0.50]
Cohesive energy $E_c$ (eV/pair)	10.64 [10.61]	10.43[10.42]
$B$ (GPa)	162 [193]	210 [260]
$V_{\text{eq},t}/V_0$	0.955	0.966
Equilibrium transition pressure	8.22	

energy-volume curves for both phases are in good agreement with prior works and are shown in Fig. 2. We predict the bulk modulus of WZ- and RS-ZnO to be  $B=162$  and 210 GPa, respectively. The bulk modulus are in reasonable agreement with the experimentally observed values of  $B=142.6$  GPa for WZ and  $B=202.5$  GPa for RS. The common tangent gives the equilibrium transition pressure between WZ and RS phases of 8.22 GPa, at a volume compression of  $V_{\text{eq},t}^{\text{WZ}}/V_0^{\text{WZ}}=0.955$ , and accompanied by a volume reduction to  $V_{\text{eq},t}^{\text{RS}}/V_0^{\text{RS}}=0.966$ , in RS, where  $V_0^X$  and  $V_{\text{eq},t}^X$  are the volume of phase  $X$  at zero and equilibrium transition pressure, respectively. The equilibrium transition pressure of 8.22 GPa is roughly in the middle of range of 6.6–10.45 GPa obtained using different computational methods.<sup>10,11</sup> Our results reconfirm that, unlike GaN and SiC, the calculated equilibrium transition pressure of ZnO is essentially equal to the observed transformation pressure of 9.1 GPa (Ref. 4) within the computational accuracy. Next, we will show quantitatively that the transformation barrier of ZnO at this pressure is much lower than the transformation threshold observed in the other two materials.

Similar to our prior work in GaN, we explicitly mapped out the energy surface as a function of two independent strain parameters,  $c/a$  and  $b/a$  varied from 1.61 to 1.00 and 1.733 to 1.00, respectively. The internal parameters  $u$  and  $v$ , are allowed to relax for each strained configuration. We have

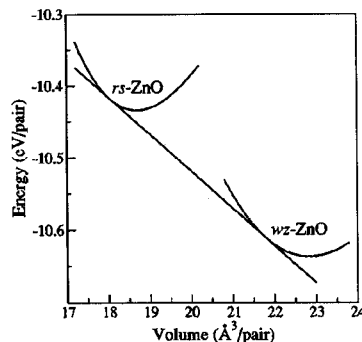


FIG. 2. The cohesive energy as a function of volume for RS- and WZ-ZnO and the common tangent construction.

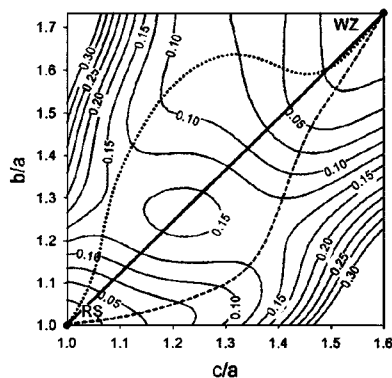


FIG. 3. Contour plot of the minimized enthalpy (with respect to  $u$ ,  $v$ , and volume, in eV/pair) as a function of  $c/a$  and  $b/a$  in ZnO under the equilibrium transition pressure  $P_{eq,T}=8.22$  GPa. Dotted (dashed) line indicates the parallel (in-plane) strain induced transformation path. Solid line indicates the straight diagonal path.

investigated a total of 104 strained configurations, corresponding to an interval of 0.05 in  $c/a$  and 0.10 in  $b/a$  in the  $c/a$ - $b/a$  space. Volume optimization is performed using at least four volumes (surrounding the minimum-energy volume) for each strained configuration. This allows us to obtain the energy-volume curve needed for calculating enthalpy under pressure for each strained configuration. To study the transformation under pressure, we calculate the enthalpy for each strain configuration and map out the enthalpy surface in the  $c/a$ - $b/a$  space. The enthalpy for each strain configuration is given by

$$\Delta H = \Delta E + p\Delta V,$$

where  $E$  and  $V$  are taken at the volume for which the enthalpy is minimized, or the external pressure  $p = -dE/dV$ , and  $\Delta$  means the difference from RS. The enthalpy surface at our calculated equilibrium transition pressure  $P=8.22$  GPa is shown in Fig. 3. We can immediately see a notably low transformation barrier of 0.15 eV. In the figure we illustrated three transformation paths in the multidimensional  $c/a$ - $b/a$  space. The first path (dotted line) corresponds to the transformation induced by a  $c/a$  strain (i.e., a parallel strain). Along this path, for each  $c/a$  we find  $b/a$  with minimum enthalpy. Following similar logic, the second path (dashed line) corresponds to the transformation induced by a  $b/a$  strain (i.e., an in-plane strain). The third path is adopted from Ref. 8, i.e., along the straight diagonal line in  $c/a$ - $b/a$  space, defined as  $[(b/a)-1]=1.20[(c/a)-1]$ . The cross sections of the enthalpy surface along all three paths clearly show the transformation barrier of around 0.15 eV (Fig. 4). The homogeneous transformation barrier of 0.15 eV in ZnO is very low in comparison to GaN (Ref. 8) and SiC.<sup>9</sup>

We repeated the process to find the transformation enthalpy barrier but at different pressures. Figure 5 shows the transformation enthalpy barrier as a function of pressure for ZnO in comparison with AlN, GaN, and SiC.<sup>9</sup> For GaN, the plot of barrier-pressure curve is read from Fig. 6 in Ref. 8. As already mentioned, both GaN and SiC do not transform at

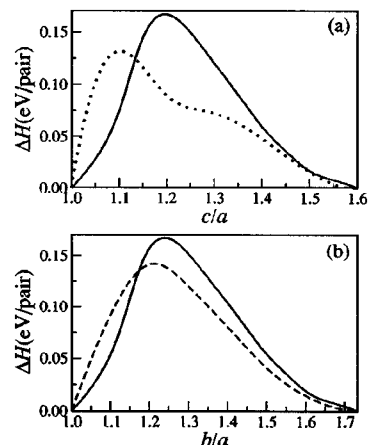


FIG. 4. Minimum enthalpy difference  $\Delta H$  at the equilibrium transition pressure  $P=8.22$  GPa along different paths: dotted line (a), parallel strain induced path; dashed line (b), in-plane strain induced path; solid lines, straight diagonal path.

their predicted equilibrium transition pressures (marked by the dashed arrows). They are observed to transform at much higher pressures (marked by the solid arrows). Since there is no prior study of barrier-pressure curve for AlN and since AlN is one of the materials that transforms at the pressure [ $P_T=22.9$  GPa (Ref. 20)] higher than its predicted equilibrium transition pressure [ $P_{eq,T}=9.2$  GPa (Ref. 21)], we calculated its barrier-pressure curve<sup>22</sup> based on the diagonal transformation path and computational detail similar to ZnO study. Remarkably, the calculated (homogeneous) transformation barriers of all three materials have about the same value of 0.25 eV/pair at their respective experimentally observed transformation pressures. This suggests that this value

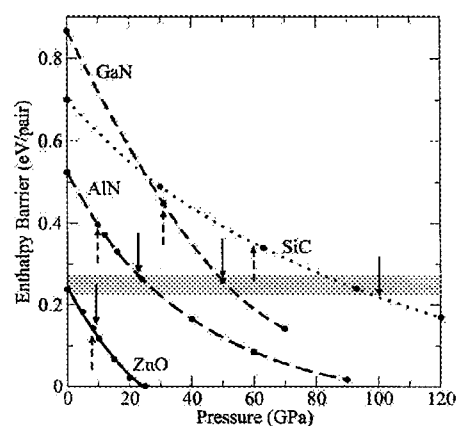


FIG. 5. Enthalpy barriers of the WZ-RS phase transformation as a function of pressure: solid line, ZnO; long dashed line, AlN; dashed line, GaN (Ref. 8); dotted line, SiC (Ref. 9). The dashed arrows indicate the calculated equilibrium phase transition pressures. The solid arrows indicate the observed phase transition pressures. The shaded area indicates a rough estimation of threshold enthalpy barrier at which the transformation takes place in AlN, GaN, and SiC.

may be considered as an empirically observed threshold barrier. Whether the same threshold barrier applies to other materials or is just a coincidence for the three materials studied will be the subjects of further studies. However, it is consistent with the fact that for ZnO, the transition can readily take place even at the equilibrium phase transition pressure, since the barrier at this pressure is already much lower than 0.25 eV.

Note that the threshold homogeneous transformation barrier of around 0.25 eV/pair (corresponding to about 3000 K) is high in comparison to the thermal energy. One should not imagine that the transformation can occur as a single homogeneous domain and use our enthalpy barrier per pair to calculate the transformation energy of the process since it will likely result in an enormous total barrier. There is clear experimental evidence that the phase transformation does not occur as a single homogeneous domain.<sup>2</sup> The magnitude of the calculated enthalpy barrier is likely related to the energy needed to create the nucleation region of the new phase before the rest of a small domain cascadingly transformed. Since the actual complicated nucleation process as well as the actual energy involved is currently unclear, the accessible

homogeneous transformation barrier serves as the second best mean to predict the transformation.

In conclusion, a detailed homogeneous WZ-RS phase transformation study of ZnO is carried out using first principles enthalpy calculations. Among the four materials with available transformation detail, ZnO is a special case for which the homogeneous transformation enthalpy barrier of 0.15 eV is lower than the apparent transformation threshold of 0.25 eV/pair obtained for the other three materials. Therefore, the transformation can readily take place at the phase equilibrium pressure. We propose that the threshold homogeneous transformation enthalpy barrier of 0.25 eV/pair could be a universal threshold barrier, but this hypothesis will need further tests on more materials and the physical meaning of this threshold value will also need further study.

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