Pressure induced zincblende to rocksalt phase transition in AlN nanocrystal

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Abstract. Structural phase transition in Aluminium nitride (AlN) nanocrystal has been studied within the framework of density-functional theory, using both the local-density as well as generalized gradient approximation as exchange correlation functionals. The study observes that under the application of pressure AlN nanocrystal transforms from its original zincblende (B3) type phase to hypothetical rocksalt (B1) type phase within the pressure range of 46GPa to 56GPa, which is comparatively larger than its bulk counterpart. The lattice parameter, bulk modulus and pressure derivatives of AlN nanocrystal in its original B3 type phase as well as hypothetical B1 type phase have also been computed as ground state properties. The mechanical strength of the AlN nanocrystal has been analysed in terms of volume collapse at transition pressure and bulk modulus.

Introduction
In the last few years, nanostructures of semiconducting materials have attracted a great attention of scientific community as they are expected to play a significant role in the development of future nanoscale technology, particularly in the optoelectronic and field-emission devices. Aluminium nitride (AlN), with its wide band gap, high thermal conductivity and high melting point can be used in various electronic applications. Lu et al.[1] have synthesized the hexagonal and cubic AlN nanocrystals with average grain size of about 2 nm and 4nm. Hexagonal AlN nanocrystals with average diameters in the 10–20 nm range have been prepared by the reaction of hexamethyldisilazane with AlCl3 under solvothermal conditions and a characteristic photoluminescence band is observed around 420nm [3]. Tolbert and Alivisatos [4, 5] are the pioneer workers in the field of high pressure structural transformation in nanocrystals, discussed the stability of CdSe nanocrystals in wurtzite and rocksalt phases and observed structural phase transformation under the application of pressure and also reported the effect of crystal size on the transition pressure. The hexagonal AlN nanocrystals have a particle size of 10 nm shows wurtzite to rocksalt phase transition at around 14.5 GPa, which is significantly lower than the transition pressure of 22.9 GPa observed for the bulk AlN by using the same technique with bulk modulus (B0) of 321 ± 19 GPa in wurtzite type phase of AlN nanocrystal, which is larger than that of the bulk AlN as B0 of 208 GPa[6]. Recently, Costales et al.[7] have investigated a periodic cluster approach to simulate AlN nanocrystal and predicted that the small-size...
nanocrystal display graphitic-like layers and nonbuckled wurtzite structure. Looking to the bulk aspects of AlN, the wurtzite to rocksalt structural phase transformation occur at around 20.91GPa and zincblende to rocksalt at around 19.69GPa [8] by using LDA, whereas in recent study of structural phase transformation in AlN nanocrystal with an average size of 10nm and 45nm by Lei et al.[9] the wurtzite to rocksalt transformation have been observed at 14.5GPa and 21.5GPa respectively. In view of above facts and researches on nanomaterials, we thought it pertinent to explore the possibility of carrying out an investigation structural transformation in AlN nanocrystal from its B3 to B1 type phase.

**Computational Method**

First principle calculations have been performed using the Atomistix Tool Kit (ATK) based on density functional theory. In the calculation, local density approximation with Perdew Zunger [10] type parameterization and the generalized gradient approximation with revised Perdew Burke Ezeroff parameterization [11,12 ] has been used. The plane wave functions are expressed by plane waves with cutoff energy 100Ryd. The Brillouin-zone (BZ) integration is performed with a Monkhorst-Pack scheme using 1x1x50 k points. The cutoff energy and the number of k points are varied to test the convergence and are found to converge within the force tolerance of 0.05eV/Å for the reported value. We have assumed roughly spherical nanocrystals and their diameter can be calculated by using the relationship of lattice parameter and number of atoms present in the nanocrystal, given elsewhere [13]. The transition pressure is evaluated by calculating ground state energy versus cell volume (E-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 scaled factors. The calculated total energy for the considered structures at different volumes around equilibrium has been fitted to the Murnaghan’s equation of state [14]. In the present calculation we have assumed the roughly spherical nanocrystal whose diameter (d) can be calculated by using the following relationship:

\[ d = \alpha \left( \frac{3N}{4\pi} \right)^{\frac{1}{3}} \]

Where, ‘\(\alpha\)’ is the lattice parameter and ‘N’ number of atoms present in the nanocrystal.

**Results and Discussions**

The present paper discusses the ab-initio study of structural phase transformation in AlN nanocrystal from its zincblende (B3) type phase to hypothetical type rocksalt (B1). The computation of total energy has been performed within the density-functional theory framework, using both the local-density and generalized gradient approximation as exchange correlation functional. To understand the ground state properties of AlN nanocrystal in its B3 and B1 type phase the equilibrium lattice parameter, bulk modulus and pressure derivatives have been computed and summarized in Table-1 along with their bulk counterpart. The computed ground state parameters for bulk AlN in its B3 and B1 type phases are in close match with the other reported values [8,15-19], whereas the calculated ground state parameters for AlN nanocrystal in its two phases could not get compared due to absence of any experimental and theoretical data. Our calculated bulk modulus and pressure derivatives for AlN nanocrystal in its B3 and B1 type phases are comparatively smaller than the bulk counterpart. The calculated total energies are plotted as a function of volume for AlN nanocrystal in B3 and B1 type phases using LDA and GGA potentials in Figure 1(a) and (b). The equilibrium volume of B1 type phase of AlN nanocrystal is lower than that of B3 type phase, as in the case of bulks. The transitions have been calculated through the two pairs of E –V curves, and the E and V values at each tangent point are listed in table 2. From the obtained energy and volume data at the points of structural transition, the volume collapse (-\(\Delta V/V_0\)) at transition pressure (\(P_t\)) has been calculated. The observed structural phase transitions from B3 to B1 in AlN nanocrystal are 46.16GPa and 55.73GPa using LDA and GGA potentials respectively, which are comparatively larger than their bulk counterpart. One of
the reasons behind this increase in transition pressure is probably the decrease in the volume collapse at the transition pressure. In the present theoretical approach we have not considered the surface energy differences and internal energy differences; otherwise these two factors also play a vital role in explaining the elevation of transition pressure. Figure 2 (a) and (b) shows the plots of relative volume as a function of pressure for AlN nanocrystal using LDA and GGA potentials, where the volume collapse at transition pressure are calculated and summarized in table 2. The calculated transition pressure and volume collapse for bulk AlN are in good agreement with the other reported data [8,15].

Figure 1(a-b). Energy vs. volume curves for AlN nanocrystal.

Figure 2. Relative volume vs. pressure curves for AlN nanocrystal.

Conclusion
The present study computes the structural phase transition in AlN nanocrystal from zincblende (B3) to rocksalt (B1) structure at high pressure and calculation found that the transition pressure of AlN nanocrystal is higher than that of the bulk AlN. The calculated lattice parameter, bulk modulus and pressure derivatives of bulk AlN in its B3 and B1 type phases are in good agreement with the other reported data.
Table 1. The calculated lattice parameter (a), bulk modulus (B₀) and pressure derivatives (B₀′) for AlN nanocrystal.

| Structure | Lattice Parameter (a) | Bulk Modulus (B₀) | B₀′ |
|-----------|----------------------|------------------|-----|
|           | B3-AlN | B1-AlN | B3-AlN | B1-AlN | B3-AlN | B1-AlN | B3-AlN | B1-AlN |
| Nanocrystal | 4.348, 4.017, 186.150, 261.341, 3.684, 4.155, | 4.515, 4.113, 134.940, 226.364, 3.197, 3.210, |
| Bulk      | 4.328, 3.993, 200.673, 276.958, 3.715, 4.887, | 4.407, 4.104, 181.016, 230.469, 3.404, 3.544, |
|           | 4.36, 4.031, 208.27, 274.87, 3.95, 4.02, | 4.38, 4.052, 197.92, 260.60, 3.91, 3.99, |
|           | 4.302, 3.978, 210, 272, 3.71, 3.815, 3.5, 0, | 4.37, 4.045, ±17, 221, 4, 18, |
|           | ±5.0, 4.8±1.0, | |

aLDA, bGGA, cRef, dRef,

Table 2. The calculated results of structural phase transition for AlN nanocrystal.

| Structure | Volume (Å³) | -ΔV/V₀ (%) | Energy (eV) | P₀ (GPa) |
|-----------|-------------|-------------|-------------|----------|
|           | B3-AlN | B1-AlN | B3-AlN | B1-AlN | B3-AlN | B1-AlN | B3-AlN | B1-AlN |
| Nanocrystal | 73.421, 57.882, 16.94, -417.062, -416.610, 46.16, | 82.166, 62.109, 18.28, -422.728, -422.034, 55.728, |
| Bulk      | 72.372, 56.991, 19.74, -417.767, -417.680, 6.324, | 76.409, 61.041, 19.85, -423.528, -422.973, 22.89, |
|           | 55.29, 20.99, 19.69, | 56.37, 20.56, 25.75, |
|           | 20.4, 7.15, | |

aLDA, bGGA, cRef,dRef.

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References
[1] Lu S X, Tong Y H, Liu Y C, Xu C S, Lu Y M, Zhang J Y, Shen D Z and Fan X W 2005 J. Phys. and Chem. of Solids 66 1609
[2] Zhang Yingjiu, Liu Jun, He Rongrui, Zhang Qi, Zhang Xiaozhong, and Zhu Jing 2001 Chem. Mater. 13 (11) 3899
[3] Sardar Kripasindhu and Rao C N R 2005 Solid State Sciences 7 217
[4] Tolbert S H and Alivisatos A P 1994 Science 265 373
[5] Tolbert S H and Alivisatos A P 1995 J. Chem. Phys. 102 4642
[6] Wang Zhongwu, Tait Kimberley, Zhao Yusheng, Schiferl David, Zha Changsheng, Uchida Hinako and Downs Robert T 2004 J. Phys. Chem. B 108 11506
[7] Costales Aurora, Blanco M A, Francisco E, Solano C J F, Pendas A Martin 2008 J. Phys. Chem. C 112 (17) 6667
[8] Saib S and Bouarissa N 2005 Eur. Phys. J. B 47 379
[9] Lei W W, Liu D, Zhang J, Cui Q L and Zou G T 2008 J. Phys.: Conf. Ser. 121 162006
[10] Perdew J P and Zunger A 1981 Phys. Rev. B 23 5048
[11] Zhang Y and Yang W 1998 Phys. Rev. Lett. 80 890
[12] Hammer B, Hansen L B and Norskov J K 1998 Phys. Rev. B 59 7413
[13] Sapra Sameer and Sarma D D 2004 Phys. Rev. B 69 125304
[14] Murnaghan F D 1944 Proc. Nat. Acad. Sci. USA 30 244
[15] Serrano J, Rubio A, Hernandez E, Munoz A, Mujica A 2000 Phys. Rev. B 62 16612
[16] Properties of Group-III Nitrides, edited by J. H. Edgar, EMIS Datareviews Series (IEE, London, 1994)
[17] Vollstadt H, Ito E, Akaishi M, Akimoto S and Fukunaga O 1990 Proc. Jpn. Acad., Ser. B: Phys. Biol. Sci. 66 7
[18] Uehara S, Masamoto T, Onodera A, Ueno M, Shimomura O, Takemura K 1997 J. Phys. Chem. Solids 58 2093
[19] Xia Q, Xia H, Ruoff, A L 1993 J. Appl. Phys. 73 8198