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Comparative studies of structural transition between AlN nanocrystals and nanowires

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Abstract. The structural transition of AlN nanocrystals and nanowires were investigated simultaneously under pressures up to 37.2 GPa by *in situ* angle dispersive high-pressure x-ray diffraction using synchrotron radiation source and a single diamond anvil cell. The size of hexagonal AlN nanocrystals and the diameter of nanowires are 45 nm on average. A pressure-induced wurtzite to rocksalt phase transition starts at 21.5 GPa and completes at 27.8 GPa for the nanocrystals and nanowires, respectively. The high-pressure behaviors of AlN nanocrystals the same as the AlN nanowires might arise from the similar size and diameter in nanocrystals and nanowires. Hexagonal AlN nanocrystals (45 nm) display an apparent volumetric contraction as compared to the AlN nanocrystals (10 nm) which might induce the difference of transition pressure.

1. Introduction

III-nitride compounds have attracted increasing attention in recent years due to their significant applications, such as optoelectronic and field-emission devices. As an important candidate of these compounds, Aluminum nitride (AlN) has various unique properties such as excellent thermal conductivity, high chemical resistance, high melting point, wide band gap and small electron affinity, which have gained considerable interests [1-5]. As for bulk AlN, high-pressure studies have proved that a pressure-induced wurtzite to rocksalt phase transition occurs at the pressure of about 20.0 GPa [6, 7]. In recent years, the high-pressure studies on nanomaterials have stimulated great enthusiasm in order to improve our understanding of the structural stability and the mechanical properties of nanomaterials [8-13]. The high-pressure measurements on AlN nanocrystals with an average crystal size of 10 nm show that the wurtzite to rocksalt phase transition starts at 14.5 GPa [14], the transition pressure is significantly lower than the bulk material. They indicated that the reduction of phase transition pressure observed results from the particle size below the critical size of 15 nm and the volumetric expansion. Since then, a similar behavior has been observed from numerous nanocrystals (e.g. TiO₂, γ -Fe₂O₃ and CeO₂) [11-13]. However, the high-pressure behavior, in particular the particle size larger than the critical size of 15 nm and the volumetric contraction, of nanocrystals is less known. Apparently more detailed experimental and theoretical works are needed to fully understand this high-pressure behavior of nanocrystals. As for AlN nanowires, our previous study [15] showed that the transition pressure at 24.9 GPa for the wurtzite to rocksalt phase transition is larger than the bulk material, we attributed distinct high pressure behaviors in AlN nanowires to unique geometry. However, there are no direct comparative high-pressure studies between AlN nanocrystals and AlN nanowires simultaneously in a single diamond anvil cell.

In this paper, we report a high-pressure study between AlN nanocrystals and nanowires simultaneously using an *in situ* angle dispersive synchrotron radiation technique in a single diamond anvil cell. The size in our AlN nanocrystals is markedly larger than the critical size of 15 nm and display an apparent volumetric contraction. This comparative subtle approach would eliminate

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systematic errors arising from instrument response using different techniques [8] and thus would allow effective detection of the indeed different high-pressure behaviors between AlN nanocrystals and AlN nanowires. The size of hexagonal AlN nanocrystals and the diameter of nanowires are 45 nm on average larger than the critical size of 15 nm. An onset pressure of 21.5 GPa from the wurtzite to rocksalt phase transition is observed in AlN nanocrystals and nanowires, respectively. Furthermore, the transition to the rocksalt phase is completed up to 27.8 GPa, which is very swift compared with the pressure-induced transition in bulk and Nanocrystals (10 nm) AlN. Such same high pressure behaviors in AlN nanocrystals and nanowires might be attributed to them with the similar size and diameter. The transition pressure of AlN nanocrystals (45 nm) is significantly larger than that in AlN nanocrystals (10 nm) and is also little larger than that in bulk AlN because of volumetric contraction.

2. Experimental details

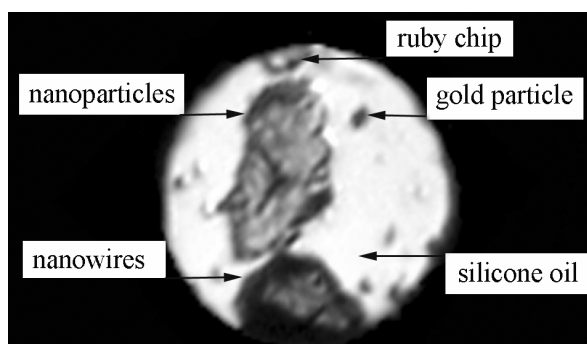


Figure 1. In-situ high-pressure optical micrograph of the AlN nanocrystals and nanowires in a single diamond anvil cell.

The AlN nanocrystals studied here were previously obtained by the dc arc plasma method through the reaction of metal aluminum (Al) with the mixture gas of nitrogen (N_2) and ammonia (NH_3) [16]. The high-density AlN nanowires were synthesized by a direct reaction of Al with 20 kPa N_2 in a closed chamber using arc discharge method [17]. The AlN nanocrystals and nanowires used here have an average diameter of 45 nm. In each case, the sample composition and phase purity were confirmed by the corresponding electron diffraction pattern analysis and powder x-ray diffraction. The pressure was generated in a diamond anvil cell with the diamonds having a culet size of $400\mu m$. The AlN nanocrystals and nanowires with the liquid quasihydrostatic pressure-transmitting medium (Silicone oil) [18, 19] were loaded into a $100\mu m$ hole drilled in a T301 stainless steel gasket, as shown in Fig. 1. A ruby chip and some gold particles were put in the sample chamber as pressure marker.

In situ high pressure x-ray diffraction measurements were performed with angle dispersive synchrotron x-ray source ($0.4074 \text{ \AA}$) of the Advanced Photon Source at the Argonne National Laboratory, Argonne, IL. The diffraction data were collected using MAR165 CCD detector. The two-dimensional (2D) data sets were integrated using the software package Fit2D to yield conventional one-dimensional (1D) powder diffraction patterns [20].

3. Results and discussion

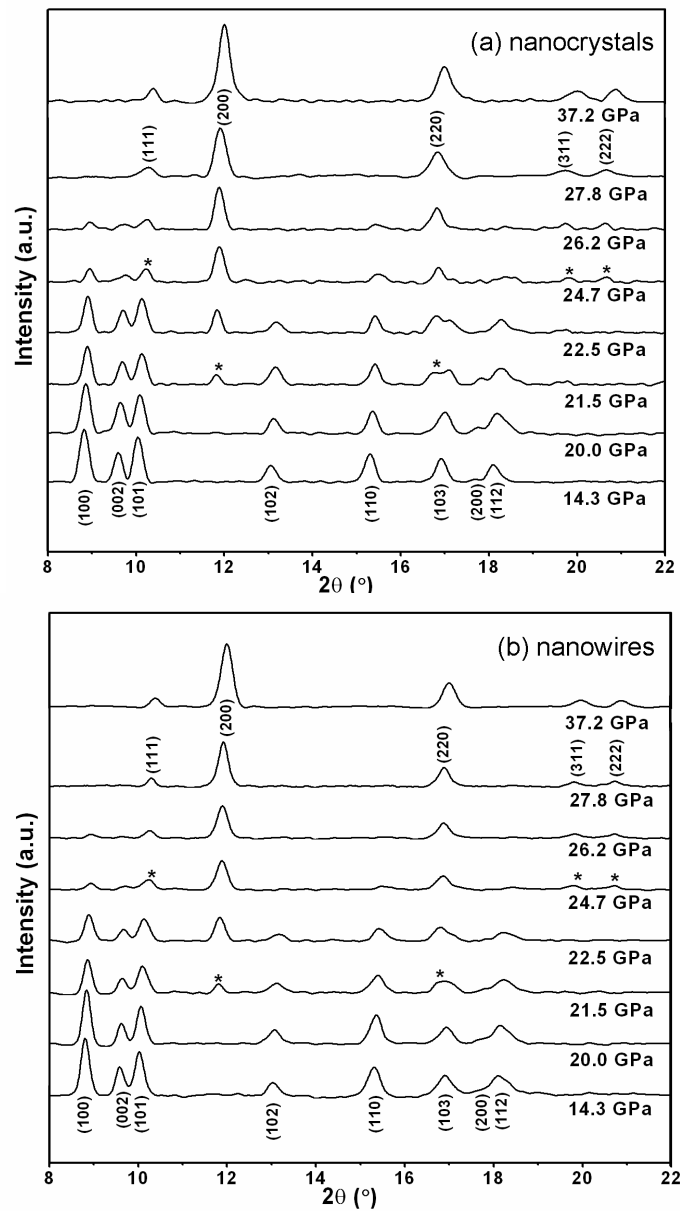


Figure 2. X-ray diffraction patterns of AlN nanocrystals and nanowires, respectively. The asterisk (*) denotes the occurrence of the new peaks of the rocksalt phase AlN.

Figure 2 (a) shows the XRD patterns of AlN nanocrystals up to 37.2 GPa. At ambient, all the diffraction peaks can be indexed to a pure wurtzite AlN crystal with lattice constants of $a=3.110$ Å and $c=4.963$ Å. The lattice parameters with corresponding unit cell volume $V_0=41.56$ Å³ are obviously smaller than those in bulk AlN macrocrystals [$a=3.111$ Å, $c=4.978$ Å, $V_0=41.72$ Å³ (Ref. 21)]. Figure 2 (b) shows the XRD patterns of AlN nanowires up to 37.2 GPa, all the diffraction peaks can be indexed to a pure wurtzite AlN crystal with lattice constants of $a=3.125$ Å and $c=4.998$ Å. The lattice parameters with corresponding unit cell volume $V_0=42.26$ Å³ are obviously larger than those in bulk AlN macrocrystals [21]. As for AlN nanocrystals and nanowires, the wurtzite phase keeps stable up to 20.0 GPa, as shown in Figure 2 (a) and (b). When the pressure reaches 21.5 GPa, a new peak of the high-pressure phase starts to appear, indicating an occurrence of the phase transition. With increasing pressure, additional diffraction peaks assigned to the high-pressure phase arise remarkably, and

meantime the diffraction peaks representing the wurtzite phase become weak. When the pressure elevates to 27.8 GPa, Figure 2 (a) and (b) show all diffraction peaks from the wurtzite phase disappear and the five obvious diffraction peaks from high pressure phase can be indexed to a cubic rocksalt phase with the unit cell parameters of $a=3.95\text{\AA}$ and $V_0=61.54\text{\AA}^3$ and $a=3.91\text{\AA}$ and $V_0=59.78\text{\AA}^3$ (four units of AlN per unit cell), respectively. As compared with the high pressure parameters in bulk AlN, AlN nanocrystals and AlN nanowires (Table 1), the transition pressure in our samples is elevated and complete phase transition is quite swift. The effect of hydrostaticity might be responsible for the small pressure range ($\sim 6\text{GPa}$) of the two coexistent phases.

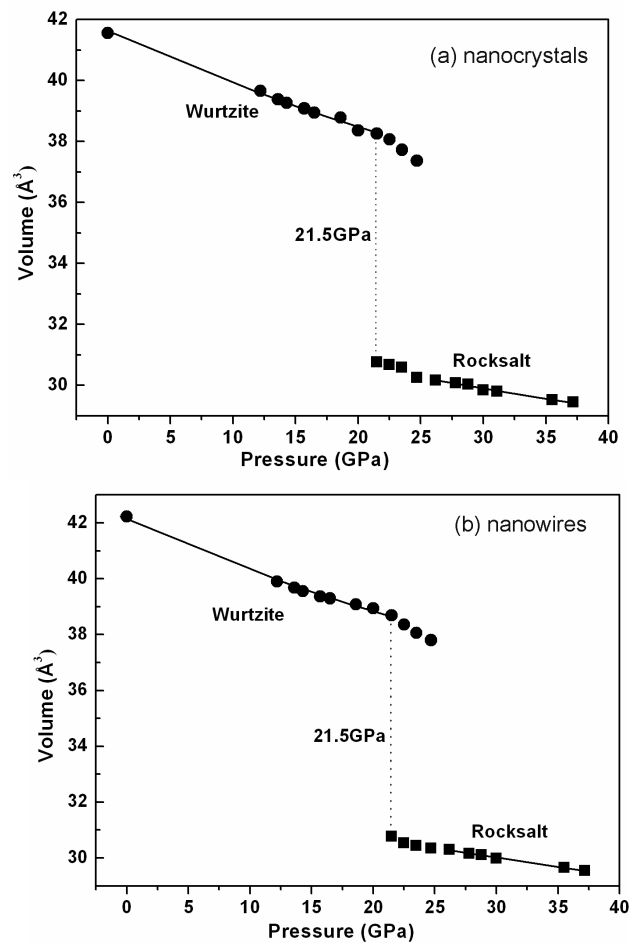


Figure 3. Pressure-volume relation of AlN nanocrystals and nanowires, respectively. The square and dot represent the wurtzite and the rocksalt phase, respectively. The line represents the fit to the Birch-Murnaghan equation.

Figure 3 (a) and (b) show the pressure-volume data of AlN nanocrystals and nanowires for both the wurtzite and rocksalt phases, respectively. It is seen that the wurtzite phase in each case still exists after the phase-transition pressure at 21.5 GPa, but the volumetric change of the wurtzite phase with the pressure became discontinuous after the phase-transition pressure. Similarly, the volume of rocksalt phase also has a big collapse at the initial transformation to rocksalt phase due to the existence of a preponderant wurtzite phase. When the pressure elevates to 26.2 GPa, the rocksalt phase is absolutely preponderant. Therefore, in the following fitting, we confine the wurtzite phase in the pressure range of 0–21.5 GPa and the rocksalt phase in the range of 26.2–37.2 GPa. The data were fitted with a third-order Birch-Murnaghan equation of state:

$$P = 3/2B_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}]\{1 + 3/4(B_0' - 4)\} \times [(V_0/V)^{2/3} - 1], \quad (1)$$

where B_0 and B_0' are isothermal bulk modulus and its pressure derivative at ambient temperature, respectively. In order to facilitate the comparison of the B_0 values, we have followed the standard procedure of setting $B_0' = 4.0$ for AlN nanocrystals and nanowires. The fitting results for wurtzite phase of AlN nanocrystals and nanowires give the bulk modulus $B_0=215.8\pm8.5$ GPa and $B_0=208.8\pm8.8$ GPa, respectively, which are close to that of bulk AlN crystals ($B_0=207.9\pm6.3$ GPa). The bulk modulus of rocksalt phase of AlN nanocrystals and nanowires are $B_0=312.6\pm22.7$ GPa, and $B_0=324.9\pm15.8$ GPa, respectively, which are a little larger than that in bulk AlN (295 ± 17 GPa) [7]. Therefore, this indicates that the reduction of particle size can significantly lead to an enhancement of the bulk modulus.

Table 1. Transition pressure (P_{TR}), completion of phase transition (P_{CO}), volume collapse at transition (P_{CO}), unit cell volume, and equation of state parameters (B_0 and B_0') of wurtzite phase of AlN nanocrystals and nanowires, respectively.

AlN morphology	P_{TR} (GPa)	P_{CO} (GPa)	ΔV (%)	V_0 (Å ³)	B_0 (GPa)	B_0'	Ref.
Bulk	20.0-22.9	31.4	17.9	41.72	207.9±6.3	6.3±0.9	6, 7
Nanocrystals(10 nm)	14.5	36.9	20.5	42.09	321±19	4	13
Nanowires (45 nm)	24.9	45.4	20.0	42.26	303.0±3.9	4	14
Nanocrystals(45 nm)	21.5	27.8	19.5	41.56	215.8±8.5	4	a
Nanowires (45 nm)	21.5	27.8	20.0	42.26	208.8±8.8	4	a

^aThis study.

We summarize our results for AlN nanocrystals and nanowires and compare them with reference data in table 1. As for AlN nanowires, our previous study reveal that P_{TR} in AlN nanowires increases greatly with the diameter of 45 nm might be due to their unique geometry. The high-pressure behaviors of AlN nanocrystals (45 nm) the same as the AlN nanowires might arise from the similar size and diameter. It was reported that a significant reduction of the phase transition pressure (P_{TR}) in AlN nanocrystals with the size of 10 nm was mainly attributed to the size-induced volume expansion at ambient conditions and softening of both the Poisson ratio and shear modulus [14]. Similarly, the phase-transition pressure has been found to decrease with the particle sizes smaller than the critical size of 15 nm for the TiO₂, γ -Fe₂O₃ and CeO₂ [11-13]. Previous studies indicate that, below the critical size, the nanocrystals typically display an apparent volumetric expansion and softening of the Poisson ratio and shear modulus, but above the critical size, they exhibit a reverse volumetric contraction [22-24]. The size in our AlN nanocrystals is markedly larger than the critical size of 15 nm and display an apparent volumetric contraction, rather than an expansion. Therefore, it can be estimated that the Poisson ratio and shear modulus might not be softened occurred in AlN nanocrystals (45 nm). It was reported that the CdSe nanocrystals with an apparent volumetric contraction exhibit an increased transition pressure [25, 26]. Thus, it is logically conclude that the P_{TR} in AlN nanocrystals (45 nm) is significantly larger than that in AlN nanocrystals (10 nm) and is also little larger than that in bulk AlN because of volumetric contraction. The higher surface energy contribution gives a considerable impact on the enhanced bulk modulus. In addition, the large bulk modulus in AlN nanocrystals and nanowires also indicate that the compressibility is less than that of bulk AlN.

4. Conclusions

In summary, we have investigated the AlN nanocrystals and nanowires to 37.2 GPa simultaneously at room temperature and at a quasihydrostatic condition by using high-energy synchrotron X-ray diffraction. The size of AlN nanocrystals and the diameter of nanowires are 45 nm on average and exhibit a noticeable volumetric contraction and volumetric expansion, respectively. A pressure-induced wurtzite to rocksalt phase transition starts at 21.5 GPa and completes at 27.8 GPa for the nanocrystals and nanowires phases, respectively, which is very swift compared with the pressure-induced transition in bulk AlN. The effect of quasihydrostaticity might be responsible for the small pressure range (~ 6 GPa) of the two coexistent phases. The high-pressure behaviors of AlN nanocrystals the same as the AlN nanowires might arise from the similar size and diameter. The bulk modulus for the wurtzite phases were determined to be 215.8 ± 8.5 GPa and 208.8 ± 8.8 GPa for the nanocrystals and nanowires, respectively, larger than that of the bulk AlN crystals with a B_0 of 207.9 ± 6.3 GPa. In contrast to the case in AlN nanocrystals (10 nm), the phase transition in AlN nanocrystals (45 nm) is significantly great. It is suggested that the volumetric contraction results in the increasing of the phase transition pressure.

Acknowledgments

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