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The structural transition of AlN nanowires was investigated under pressures up to 51.1 GPa by *in situ* angle dispersive high-pressure x-ray diffraction using synchrotron radiation source and a diamond anvil cell. A pressure-induced wurtzite to rocksalt phase transition starts at 24.9 GPa and completes at 45.4 GPa. The high-pressure behaviors of AlN nanowires differing from the bulk and nanocrystal AlN might arise from the intrinsic geometry in nanowires. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2358125]

AlN is an important III–V semiconductor for future applications in optoelectronic and field-emission devices due to its wide band gap, high thermal conductivity, high hardness, and small electron affinity.[1–4] High-pressure studies have proved that a pressure-induced wurtzite to rocksalt phase transition in bulk AlN occurs at the pressure of about 20.0 GPa.[5–7] In recent years, the high-pressure studies on nanocrystalline materials have stimulated great enthusiasm because the size of the nanoparticles has a significant effect on the phase transition and the compressibility. Generally, bulk modulus and phase-transition pressure increase with decreasing particle size.[8,9] However, 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.[10] This transition pressure is much lower than that in bulk AlN. At present, synthesis and characterization of one-dimensional nanowires attract much attention because of their unique optoelectronic and mechanical properties. However, there are few high-pressure studies on nanowires. In this letter, we report a high-pressure study on AlN nanowires using an *in situ* angle dispersive synchrotron radiation technique in a diamond anvil cell. An onset pressure of ~24.9 GPa from the wurtzite to rocksalt phase transition is observed in AlN nanowires. The transition pressure is much larger than that in nanocrystalline AlN although they have similar bulk modulus and volume expansion at ambient as well as volume collapse at the phase transition. Furthermore, the transition to the rocksalt phase is completed up to 45.4 GPa, which is very sluggish compared with the pressure-induced transition in bulk AlN. Such distinct high-pressure behaviors in AlN nanowires might be attributed to their unique geometry.

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.[11] The AlN nanowires used here have an average diameter of 45 nm and a length of several micrometers, as shown in Fig. 1. The pressure was generated in a diamond anvil cell with the diamonds having a culet size of 500 μm. The AlN nanowires with the liquid quasihydrostatic pressure-transmitting medium (methanol/ethanol/water=16:3:1) were loaded into a 100 μm hole drilled in a T301 stainless steel gasket. A ruby chip with a diameter of about 5 μm was put in the sample chamber and the pressure

was determined using a ruby fluorescence method. The *in situ* high-pressure x-ray diffraction (XRD) measurement was performed with angle dispersive synchrotron x-ray source (0.4066 Å) at beamline X17-C of National Synchrotron Light Source, Brookhaven National Laboratory. The Bragg diffraction rings were recorded with an imaging plate detector and the XRD patterns are integrated from the images with FIT2D software.

Figure 2 shows the XRD patterns of AlN nanowires up to 51.1 GPa. At ambient, 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 Å^3 are obviously larger than those in bulk AlN macrocrystals [a=3.111 Å, c=4.978 Å, V_0=41.72 Å^3 (Ref. 12)]. Some studies reveal that a volume expansion in nanoparticles is usually observed below a critical particle size of about 15 nm at ambient.[13–15] In our experiment, the size of AlN nanowires is obviously greater than 15 nm, but it also exhibits obviously volume expansion. Such a phenomenon might be related to the inherent geometry in nanowires. The wurtzite phase keeps stable up to 23.7 GPa, as shown in Fig. 2. When the pressure reaches 24.9 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
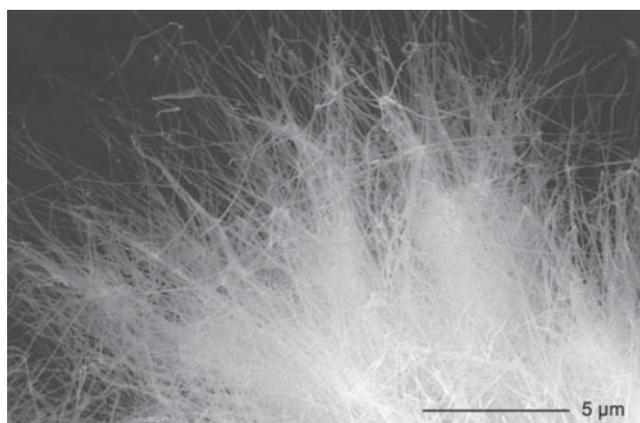

FIG. 1. Scanning electron microscopy image of the as-synthesized AlN nanowires.

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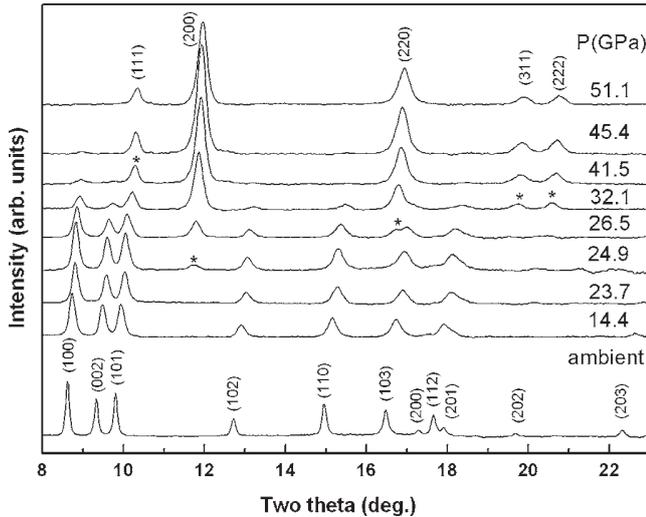
89, 141903-1

FIG. 2. X-ray diffraction patterns of AlN nanowires at different pressures. The asterisk (*) denotes the occurrence of the new peaks of the rocksalt phase AlN.
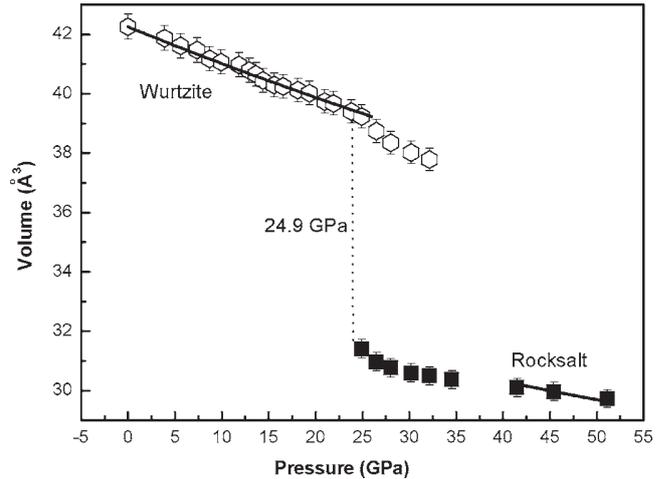

FIG. 3. Pressure-volume relation of AlN nanowires. The open hexagon represents the wurtzite phase. The solid squares represent the rocksalt phase. The line represents the fit to the Birch-Murnaghan equation. The error bar is 1%.

45.4 GPa, 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 $a=3.91$ Å and $V_0=59.78$ Å^3 (four units of AlN per unit cell). As compared with the high-pressure parameters in bulk AlN (Table I),[6,7] the transition pressure in AlN nanowires is elevated and complete phase transition is quite sluggish. The sluggishness might be explained as a high-energy hindrance that prevents the rapid transition to high-pressure phase in nanomaterials.[8,15] Moreover, the effect of nonhydrostaticity might be responsible for the wide pressure range ($\sim$20 GPa) of the two coexistent phases. When the pressure is released from 51.1 GPa to ambient, the rocksalt phase is completely preserved. This indicates that the pressure-induced transition is completely irreversible. At ambient, the cell parameters of the rocksalt phase were calculated to be $a=4.064$ Å and $V_0=67.14$ Å^3. The unit cell volume is 1.36% larger than that in rocksalt phase AlN microcrystal.[7] It should be noted that the unit cell volume of the rocksalt AlN nanocrystal at ambient has no significant difference from that of rocksalt AlN microcrystal, which may be explained by a pressure-induced increase of particle size.[10] Thus it can be estimated that the pressure did not induce an increase of size in AlN nanowires.

Figure 3 shows the pressure-volume data for both the wurtzite and rocksalt phases. It is clearly observed that the wurtzite phase still exists in a quite wide range after the phase-transition pressure at 24.9 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 41.5 GPa, the rocksalt phase is absolutely preponderant. Therefore, in the following fitting, we confine the wurtzite phase in the pressure range of 0–24.9 GPa and the rocksalt phase in the range of 41.5–51.1 GPa. The data were fitted with a third-order Birch-Murnaghan equation of state:

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

where B_0 is the bulk modulus and B_0' is pressure derivative.

The fitting result for wurtzite phase gives the bulk modulus $B_0=303.0\pm3.97$ GPa at a fixed $B_0'=4$, which is close to that of AlN nanocrystals ($B_0=321\pm19$ GPa, $B_0'=4$) and significantly greater than that of bulk AlN crystals ($B_0=207.9\pm6.3$ GPa). This indicates that the nanosized diameter in AlN nanowires significantly increases the bulk modulus. The bulk modulus of rocksalt phase is 319.2 ± 7.6 GPa at a fixed $B_0'=4$, which is a little larger than that in bulk AlN (295 ± 17 GPa).[7]

The comparison of the high-pressure parameters in bulk and nanocrystalline AlN and AlN nanowires is listed in Table I. It was reported that a significant reduction of the phase-transition pressure (P_T) 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.[10] However, P_T in AlN nanowires increases greatly, though the volume of wurtzite AlN nanowires has obvious expansion at ambient. In addition, a

TABLE I. Transition pressure (P_T), completion of phase transition (P_C), volume collapse at transition (P_C), unit cell volume, and equation of state parameters (B_0 and B_0') of wurtzite phase.

AlN morphology	P_T (GPa)	P_C (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 and 7
Nanocrystals	14.5	36.9	20.5	42.09	321±19	4	9
Nanowires	24.9	45.4	20.0	42.26	303.0±3.97	4	a

[a]This study.

large volume collapse at the transition pressure leads to a reduction of the phase-transition pressure in CeO_2, TiO_2, and Fe_2O_3 nanocrystals.[13–15] As shown in Table I, the volume collapse (ΔV) in AlN nanowires is close to that in AlN nanocrystals but larger than that in bulk AlN. That is, a large volume collapse in AlN nanowires also does not lead to a reduction of P_T. Based on the above discussions, the volume expansion at ambient and the volume collapse at transition cannot induce the reduction of P_T in AlN nanowires. The distinct high-pressure behaviors in AlN nanowires might be due to their unique geometry. This can be explained as follows: The diameter in AlN nanowires has an average size of about 45 nm and the axial lengths in AlN nanowires have several tens micrometers. The size in AlN nanowires is markedly larger than that in AlN nanocrystals and is also larger than the critical size of 15 nm, below which the volume expansion together with the softening of both the Poisson ratio and shear modulus appears in some nanocrystals.[16–18] In addition, the large bulk modulus in AlN nanowires also indicates that the compressibility is less than that of bulk AlN. Therefore, it can be estimated that the Poisson ratio and shear modulus might not be softened though volume expansion occurred in AlN nanowires. As a result, the P_T in AlN nanowires is significantly greater than that in AlN nanocrystals and is also little larger than that in bulk AlN because of volume expansion.

In conclusion, high-pressure studies on AlN nanowires show a sluggish transition from the wurtzite to rocksalt phases with a relatively high onset transition pressure of 24.9 GPa. In contrast to the case in AlN nanocrystals, the large volume expansion at ambient and volume collapse at the transition pressure cannot lead to a reduction of the phase-transition pressure. Such a unique high-pressure phenomenon might be due to the intrinsic geometry in nanowires.

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