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High-pressure structure of gallium nitride: Wurtzite-to-rocksalt phase transition

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High-pressure energy-dispersive x-ray-diffraction studies were carried out on the III-V compound gallium nitride to 70 GPa using a synchrotron x-ray source. A pressure-induced first-order phase transition from a wurtzite structure to a rocksalt structure was observed to begin at a pressure of 37 GPa.

The III-V nitrides are important in electronics, microelectronics, and materials science. Due to their small lattice constant, they are large band-gap semiconductors with large hardness and have attracted extensive theoretical and experimental interest.[1-8] Many properties of semiconductors can be scaled by atomic volume and Phillips ionicity.[9] The Van Vechten theory[10] was established based on this idea and has been successfully used for understanding the properties of a great number of the tetrahedrally coordinated semiconductors. It is widely believed that the ionicity, or charge transfer, dictates to a large extent the structural forms of high-pressure phases of III-V and II-VI compounds. Thus, the more covalent materials, i.e., the most III-V semiconductors, transform predominantly to a tetragonal β-Sn structure under pressure while the more ionic materials, i.e., the II-VI semiconductors, transform to a cubic rocksalt structure.[11] GaN is characterized by its high ionicity of 0.5 (Ref. 10) or 0.43 (Ref. 12), the highest among III-V compounds. GaN also has a large saturated electron drift velocity,[13] high thermal conductivity, and hardness. It can be used for making electroluminescent diodes and a power amplifier. With the cubic zinc-blende structure, if it exists, it is expected to have an even higher saturated drift velocity and its growth has received more interest recently.[5] However, it is not clear, so far, which cubic form GaN may have. Ultrahigh pressure is a very efficient way to tune interatomic distances in condensed matter and we expect interesting results from the high-pressure study of structural properties of GaN. The high-pressure study of GaN can also result in interesting tests of different theoretical predictions concerning general trends in behaviors of III-V and II-VI materials.[8] Therefore, it is of both physical and industrial interest to investigate the crystal structural properties of GaN under high pressure.

At ambient pressure, GaN crystallizes in a hexagonal (wurtzite) structure with space group $P6_3mc$ (C_{4v}^6) and lattice constant $a = 3.19$ Å and $c/a = 1.627$.[14] It has four atoms in the unit cell and the atomic volume is only about half of that of GaAs. It has a mixture of covalent bonding and ionic tetrahedral bonding and has a direct electronic band gap of 3.5 eV at the Γ point. The early theoretical work by Van Vechten[10] predicted that there is a phase transition to the metallic β-Sn structure at 87 GPa. Recent x-ray-absorption spectroscopy and Raman-scattering measurements[2] on GaN indicated a phase transition around 47 GPa; the crystal structure of the high-pressure phase has remained, so far, unknown. Various theoretical approaches[1,3,5,8] to the high-pressure structure of GaN, based on the *ab initio* pseudopotential method and local-density approximation[15] or linear-muffin-tin-orbital theory, have been made recently. According to these theories, the possible candidates of the high-pressure phase of GaN are NiAs (D_{6h}^4), rocksalt (O_h^5), zinc-blende (T_d^2), β-Sn (D_{4h}^{19}), and CsCl (O_h^1) structures. Some recent theoretical calculations[3,5] predicted that the most favorable high-pressure phase of gallium nitride is the rocksalt structure.

In this paper we present the structural study of GaN under ultrahigh pressure using diamond-anvil techniques and a synchrotron x-ray source. A first-order phase transformation from a wurtzite to a rocksalt structure was discovered. The observation of the rocksalt structure in GaN under ultrahigh pressure gives the first experimental evidence of a pressure-induced structural sequence from a fourfold-coordinated wurtzite crystal structure to a sixfold-coordinated rocksalt crystal structure in III-V nitride compounds.

More details of the experimental apparatus and techniques can be found in Refs. 16–19. We used a diamond-anvil cell with anvil tips 300 μm in diameter and drilled a sample hole 100 μm in diameter on a preindented spring steel gasket of 50-μm thickness. Polycrystalline GaN with 99.99% purity was placed in a sample region of 100 μm in diameter. Two different experiments were performed on the GaN sample. The first employed gold as an internal pressure marker while the second was done with only GaN in the sample hole to avoid the interference due to the marker material. The sample pressure in the first experiment was determined by the x-ray diffraction of gold powder mixed with the GaN sample, and the isothermal equation of state of gold is given by Jamieson, Fritz, and Manghnani.[20] In the second experiment pressures were calculated from the equation of state of GaN obtained from the first experiment.

The energy-dispersive x-ray-diffraction (EDXD) data of GaN were collected at the Cornell High Energy Synchrotron Source. The diffraction angle (2θ) was set at 15°, which corresponds to an Ed (the x-ray photon energy times the d spacing of the polycrystal sample) of 34.7 keV Å. At low pressures, the x-ray-diffraction spectra taken at different locations of GaN sample showed a very strong texture in the sample. Such a strong texture in diffraction intensity is believed to be caused by particle size effect and high ionicity of GaN. The texture of the GaN sample was also checked and confirmed by x-ray diffraction of the sample loaded in a capillary. Figures 1(a) and 1(b) show the two room pressure EDXD spectra taken at two different locations (*A* and *B*) of the GaN sample in a diamond anvil cell. The large difference in the intensities of the correspondent diffraction peaks shown in spectra *A* and *B* is due to the texture in the GaN sample. However, all the *d* spacings calculated from the x-ray-diffraction spectra fit well to the known hexagonal wurtzite structure in spite of the discrepancy in intensity fitting. The measured room pressure lattice parameters *a* of 3.19 Å and c/a of 1.626 are in agreement with the known result.[14] At each pressure loading, we took several spectra at different locations of the sample region in order to check the texture of the sample. A structural phase transformation was observed beginning at 37 GPa. This transition pressure is lower than the result obtained in the previous x-ray-absorption experiment.[2] The x-ray-diffraction pattern shown in Fig. 2(a) is a mixture of primarily the wurtzite phase with some rocksalt phase of the GaN sample at 37 GPa. Upon further increasing pressure, the x-ray-diffraction spectra showed only the peaks of the rocksalt structure [Fig. 2(b)]. Fourteen diffraction lines were observed at a pressure of 50 GPa and all fit well to the rocksalt structure. Table I shows the fit of the diffraction peaks to the rocksalt gallium nitride with a lattice parameter of $a=4.006\pm0.001$ Å. All the diffraction peaks are fitted to a Gaussian function with a linear background. It is interesting to point out that the sample texture vanished after the phase transformation. The disappearing of the sample texture after the phase transformation may be due to the formation of many new crystals in the GaN sample during the large collapse of volume associated with the wurtzite-to-rocksalt phase transition. This is a structural phase transformation from a low-symmetry crystal structure to a high-symmetry crystal structure. The GaN sample remained in the rocksalt structure to at least 70 GPa, the upper pressure limit of the experiment. During unloading, the wurtzite structure began reappearing at about 25 GPa (although it may have appeared sooner but no data were taken above this pressure) and returned completely back to the wurtzite structure after releasing the sample pressure. The earlier x-ray appearance near-edge structure study[2] showed that the reversal transition begins at 30 GPa. Hence, the equilibrium transformation pressure P_{eq} is within the interval

$$30\ \mathrm{GPa} \leq P_{\mathrm{eq}} \leq 37\ \mathrm{GPa}\ . \tag{1}$$

The Ga-Ga distances of the GaN sample in wurtzite and rocksalt phases during the phase transformation are 3.03 ± 0.02 Å and 2.84 ± 0.02 Å at 40 GPa, which are obtained by using the lattice parameters calculated from the x-ray-diffraction data collected in this experiment. We note that such a decrease in the Ga-Ga distance during the wurtzite-to-rocksalt phase transformation is triggered by the pressure-induced charge transfer (associated with the changing in the ionicity[9] and electronegativity[21] of the GaN sample).

From the x-ray-diffraction spectra, the reduced volume V/V_0 of GaN versus pressure (equation of state) was cal-

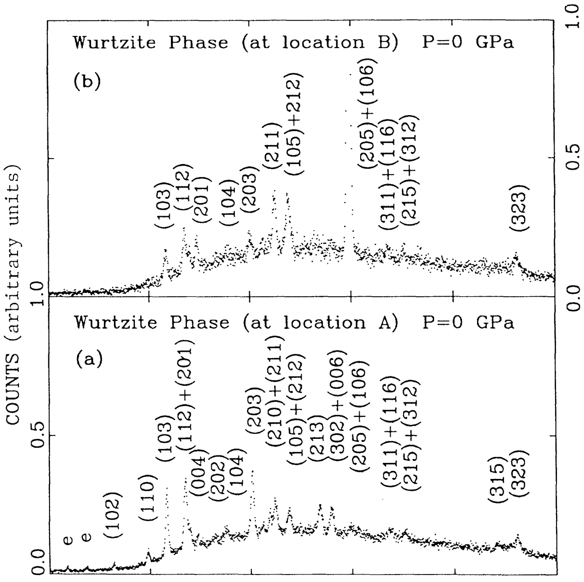

FIG. 1. Room pressures and room-temperature energy-dispersive x-ray-diffraction (EDXD) spectra of the GaN sample taken at different locations (*A* and *B*) of the sample ($Ed=34.691\pm0.006$ keV Å). The large discrepancy in the intensities of diffraction peaks is believed due to the strong texture in the GaN powder sample. The symbols *e* are escape peaks of the Ge detector from strong GaN diffraction lines.

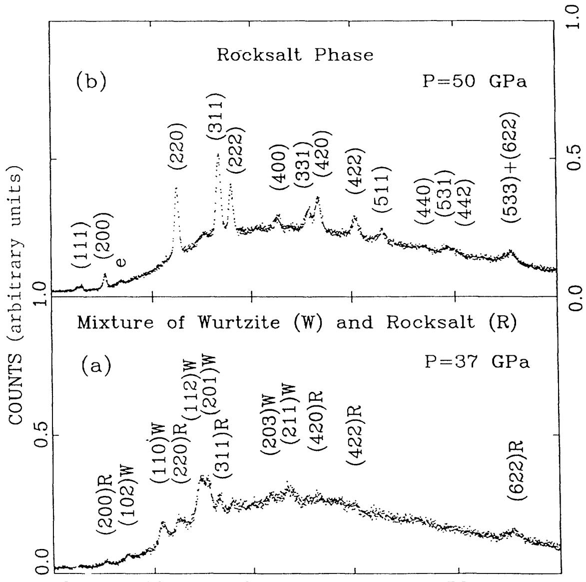

FIG. 2. Energy-dispersive x-ray-diffraction spectra of the GaN sample taken during pressure loading ($Ed=34.691\pm0.006$ keV Å). (a) The EDXD spectrum taken at 37 GPa which shows the mixture of wurtzite and rocksalt phase. (b) The EDXD spectrum taken at 50 GPa which shows the rocksalt phase after the phase transformation. The symbols *e* are escape peaks of the Ge detector from strong GaN diffraction lines.

TABLE I. The measured and calculated d spacings of rocksalt GaN at 50 GPa ($Ed = 34.691 \pm 0.006$ keV Å).

hkl	d_{exp} (Å)	d_{calc} (Å)	$\Delta d/d$ (%)
111	2.308	2.313	0.22
200	2.003	2.003	0.01
220	1.416	1.416	0.01
311	1.207	1.207	0.04
222	1.158	1.157	−0.12
400	1.001	1.002	0.11
331	0.919	0.919	0.02
420	0.896	0.896	−0.03
422	0.818	0.818	−0.06
511	0.770	0.771	0.11
440	0.707	0.708	0.19
531	0.678	0.677	−0.10
442	0.667	0.667	0.08
620	0.632	0.633	0.18
622	0.604	0.604	0.00

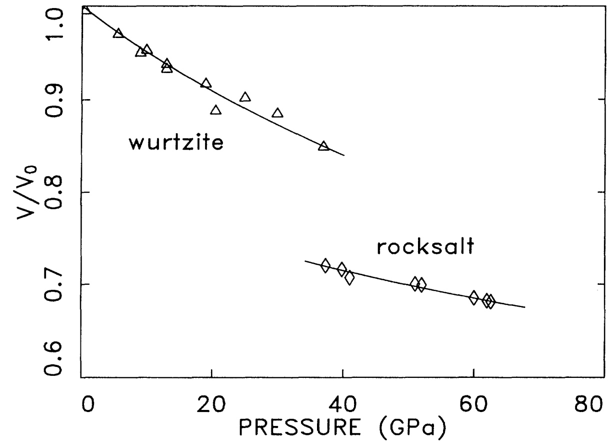

FIG. 3. The measured equation of state of the wurtzite and rocksalt phases of GaN. The solid curves are the fits of the Birch first-order equation of state to the data (see text for details).

culated and is shown in Fig. 3. The data were fit to a Birch first-order equation of state,[22]

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

where $x = V_N/V$, V is the volume per atom at pressure P, V_N is a fitting parameter which corresponds to the extrapolated volume per atom of the phase under consideration at zero pressure, B_0 is the isothermal bulk modulus at zero pressure, and B_0' is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure. The fits to the wurtzite and rocksalt phases of GaN to the Birch first-order equation of state are shown by the solid curves in Fig. 2. The calculated coefficients of the Birch first-order equation of state for the wurtzite phase are $B_0 = 188$ GPa and $B_0' = 3.2$, and for the rocksalt phase are $B_0 = 248$ GPa and $B_0' = 5.5$. These values are in agreement with the results of recent x-ray-absorption measurements[2] and are slightly higher than the results from theoretical calculations using the local-density-functional methods.[5] The fitting parameter V_N/V_0 of the rocksalt GaN is 0.83 ± 0.02. From the intrapolations of the Birch first-order equations of state of different phases to the corresponding transition pressures, the volume decreases during the transformations $(V_{\mathrm{I}} - V_{\mathrm{II}})/V_{\mathrm{I}}$ (where V_{I} and V_{II} are volume per atom just before and just after phase transformation of GaN) are calculated to be about 17.0% at 37 GPa (or at a volume fraction of 0.85 of the wurtzite phase).

The discovery of the rocksalt phase in GaN under high pressure, from the crystal structural point of view, gives the first experimental evidence of a pressure-induced structural sequence in III-V nitrides from a fourfold-coordinated wurtzite structure to a sixfold-coordinated rocksalt structure. The *ab initio* density-functional theory based on the nonlocal pseudopotential method has been applied to GaN.[3,5] Further *ab initio* density-functional calculations on the change with pressure of the ionicity of both wurtzite and rocksalt GaN, based on the present experimental data and Philip's scaling theory, are needed to investigate the electronic and structural properties of GaN at higher pressures. An optical study will also be of interest to understand the closing of direct and indirect band gaps in GaN. We expect that, with current megabar pressure capability of diamond-anvil cells, similar pressure-induced structural sequences can be experimentally studied for other III-V nitrides such as AlN, InN, and possibly BN.

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