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Raman scattering and absorption study of the high-pressure wurtzite to rocksalt phase transition of GaN

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The high-pressure wurtzite to rocksalt phase transition of high quality epitaxial GaN has been studied using Raman scattering and optical absorption spectroscopy. The results are compared with *ab initio* calculations performed within the framework of density functional theory. The Raman scattering due to the phonon modes of the wurtzite phase was followed up to 69 GPa; the phase transition was marked by the appearance of new features which we assign to disorder activated, symmetry forbidden, scattering from the rocksalt phase. There is no evidence for the recently proposed metallic MgO-*h* intermediate phase. Absorption measurements show an absorption feature at 1.7 eV for the rocksalt phase at 69 GPa.

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Crystalline semiconductors and insulators usually adopt a crystal structure that reflects the relative degree of covalency of the compound. In this respect the study of the high-pressure phase transitions of such compounds reveals details of the chemical bonding trends in such materials. More recently there has been growing interest in the observation and understanding of the actual transition mechanisms. One of the most widely studied transitions amongst the $A^{N}B^{8-N}$ semiconductors is from the tetrahedrally bonded sphalerite or wurtzite structures to the octahedrally bonded rocksalt structure. For these materials, first principles calculations almost universally predict a transition sequence for the more-ionic compounds tetrahedral structure—rocksalt—CsCl.[1] However, recent experimental studies have found significant deviations for this behavior, with the absence of some phases in some cases of the presence of extra phases in others; with a direct transition to the β-Sn structure being preferred by highly covalent materials.[2] The presence of extra, sometime metastable, intermediate phases is also attracting interest. Limpijumnong *et al.*[3] recently suggested an intermediate orthorhombic phase for GaN using first principles theoretical techniques.

GaN is a wide band gap semiconductor of great technological importance; as such its physical properties have been widely studied. In common with other strongly ionic compound semiconductors; GaN exhibits the phase transition from a wurtzite structure to rocksalt structure at high pressures. It was recently proposed that this phase transition could occur via a metallic MgO-*h* intermediate phase deformation path. In this article we report a careful Raman and absorption study of this phase transition performed with the intention of observing the presence of any intermediate phase either through the vibrational Raman spectrum or the presence of a semimetallic optical response within the pressure range of the transition. We also demonstrate the use disorder activated Raman scattering form defected crystalline structures for the study of their high-pressure phase transitions.

The high-pressure phases of GaN have been the subject of several previous studies. The techniques used have been either x-ray diffraction or Raman scattering. The samples have invariably been bulk (typically vapour phase grown) GaN crystals. Some previous Raman studies on epitaxial GaN have been reported, but these studies have been restricted to relatively low pressures (<15 GPa). The processing of GaN epilayers for loading into a diamond anvil cell (DAC) apparatus using standard mechanical polishing techniques is problematic due to the use of sapphire substrates; for the present work an excimer laser lift-off technique is used to allow the removal of thin ($1-3\ \mu$m), high quality, epilayers of GaN from a sapphire substrate.[4]

The sample studied was a GaN epilayer grown on (0001) sapphire substrates by low-pressure metalorganic vapor phase epitaxy. An excimer laser-assisted debonding technique was then employed to detach the epilayers from the substrate as described in detail elsewhere.[4] The resulting fragile membranes are left with a thin film of gallium over the detached GaN buffer surface. For this reason spectroscopy was generally performed from the top surface.

Small c. 20 μm^2 pieces of epilayer were then cleaved and loaded into a Mao-Bell-type of DAC using diamonds with 250 μm culets. The pressure was monitored by the ruby fluorescence technique using the λ^5 power law.[5] The pressure medium used was either silicon oil or 4:1 methanol/ethanol mixture. It was found that the pressure media was not completely hydrostatic with a variation of the order of 2% in the pressure over the volume of the cell, however, this does do not substantially affect the results discussed here. The Raman measurements were conducted using a Raman microscope using the 514 nm line of an Ar^+ laser or the 442 nm line of a He-Cd laser.

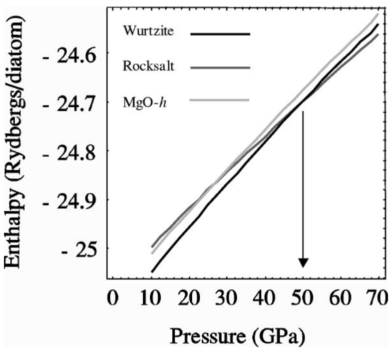

FIG. 1. Enthalpy dependence on pressure of the three phases MgO-*h*, rocksalt, and wurtzite.

Phonon frequencies and vibrational density of states (DOS) were calculated from first principles within the framework of density functional theory and the local density approximation (LDA) using the “plane wave self consistent field” (PWSCF) code.[6] Norm conserving pseudopotentials of the Troullier-Martins form were employed with the gallium 3*d* electrons treated as core with nonlinear core correction. We applied the Perdew-Zunger parameterisation of the exchange-correlation. We used a plane wave cut-off energy of 75 Ry and $4\times4\times2$ mesh of special points in the Brillouin-zone integration. At each pressure the wurtzite structure was relaxed with respect to the wurtzite c/a and u lattice parameters. This was found to give a lattice constant and c/a ratio with 1.5% of the experimental values and zone center phonon frequencies to within 5% of measured values.

Figure 1 shows the predicted enthalpy dependence on pressure in the range 0–70 GPa for the three phases, the wurtzite, rocksalt, and the (projected) MgO-*h* structure. It can be seen that our LDA calculation predicts that wurtzite to rocksalt phase transition should occur at 50 GPa, the MgO -*h* phase is not predicted to be energetically favoured over either the rocksalt or wurtzite phase at any pressure in this range. The predicted phase transition energy is somewhat above that predicted in Ref. 3 but in line with those of Ref. 7. We note that calculations based on the LDA generally overestimate transition pressures.[8]

The GaN wurtzite structure has 4 Raman active phonon modes at the Γ-point belonging to the A_1, E_1, and E_2 irreducible representations of the point group. When the long range Coulomb field is included we have two Raman active E_1 modes with zero pressure frequencies of (LO) and (TO), two A_1 modes (LO) and (TO) and two hexagonal E_2 modes with frequencies (E_2 high) and (E_2 low). There have been several previous studies of the pressure dependence of these modes;[9,10] we have followed the evolution of the 4 higher frequency modes in our epitaxial GaN samples up to 44 GPa. The resulting measured shifts and calculated dependencies are shown in Fig. 2. The measured phonon shifts are in almost perfect agreement with those observed by Perlin *et al.* in Ref. 9. Due to the limitations of the spectrometer used, it was not possible to observe the mode softening of the E_2^{low} mode. The softening of a phonon mode can, in some instances, be related to a pressure induced phase transition. In the case of GaN, the phase transition occurs before the mode becomes a true “soft mode.”[11]

Figure 3 shows a series of Raman spectra recorded at pressures up to 69 GPa. The inset images show the sample under back illumination before the phase transition (at 3 GPa) and after it is completed at 62 GPa. The intensity of the light was increased for ease of observation of color change. It can be seen that the phase transition is marked in the Raman spectrum by the appearance of a broad series of vibrational bands in the region 300–900 cm^{-1}. We demonstrate below that this is due to a disorder activated rocksalt density of states; it is clear, however, the phase transition begins around 42 GPa and is complete by 49 GPa. These values correspond well to those reported in Ref. 12 by x-ray diffraction, although in that work the diffraction peaks in the transition range itself could not be observed. During the phase transition the sample visually darkened and reddened.

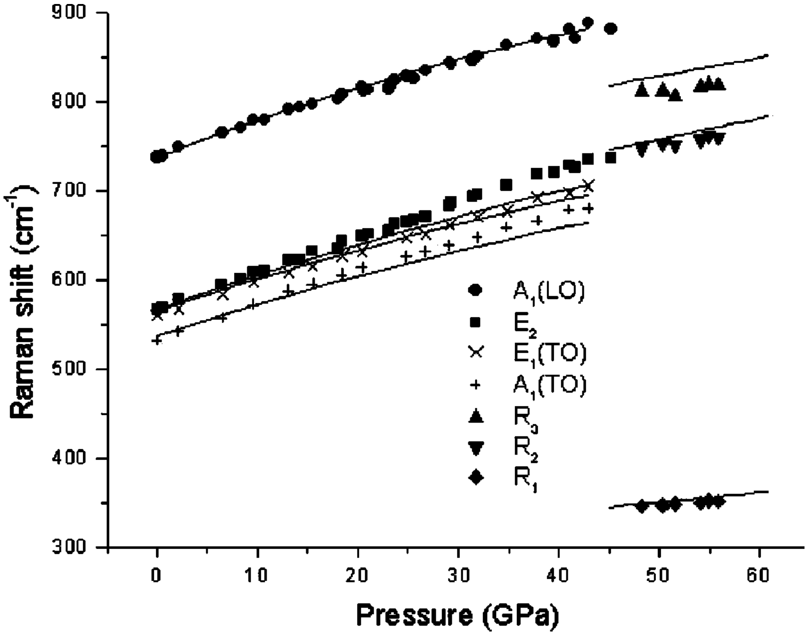

FIG. 2. Pressure dependence of phonon modes of wurtzite GaN and rocksalt GaN. The points labelled R_1,R_2, and R_3 refer to the features shown in Fig. 5. The solid lines are calculated pressure shifts using the pseudopotential model described in the text.

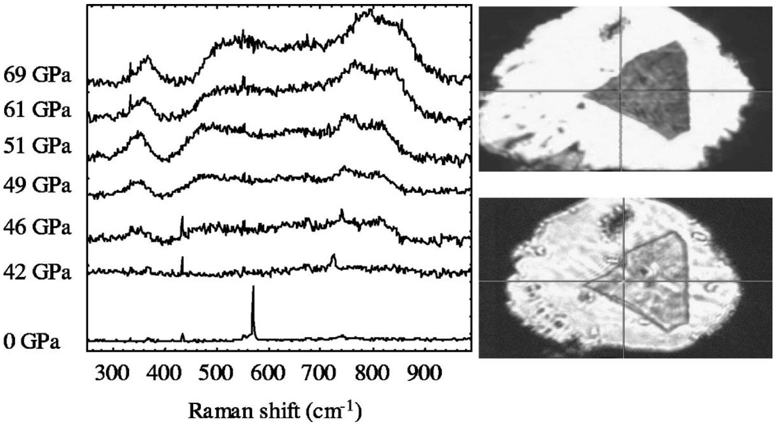

FIG. 3. A series of Raman spectra recorded at pressures up to 69 GPa. The images show the sample under back illumination before the phase transition (at 3 GPa) and after it is completed at 62 GPa.

In Ref. 9 it was reported that bulk platelets of GaN became opaque at the transition pressure and that Raman scattering could not be observed at pressures above this. We believe that our use of thin high quality epitaxial GaN creates fewer optically active defects in the resulting rocksalt material and allows the observation of transmission through the sample. The broad vibrational bands we observe in the Raman spectra are clearly coming from the rocksalt structure which has a centre of inversional symmetry and should therefore have no Raman active phonon modes. However, vibrational Raman scattering has been reported for both the $\mathrm{Mg}_x\mathrm{S}_{1-x}\mathrm{Se}$ and $\mathrm{KCl}_x\mathrm{Br}_{1-x}$ insulator alloys with rocksalt structure.[13,14] In these cases the alloy disorder relaxes the $k=0$ selection rule and gives rise to a spectrum which is essentially a phonon density of states (DOS) with the optical phonons modes in the vicinity of the X point giving rise to strong scattering as they belong to the A_{1g} Raman-allowed irreducible representation of the point group. In Fig. 4 we show the phonon dispersion curves of the GaN rocksalt phase calculated by the PWSCF code for the main high symmetry axes of the fcc Brillouin zone. It can be seen from the figure that, unlike the wurtzite (and MgO-*h* phase discussed below) the Rocksalt phase has no acousto-optic gap in it density of states. In Fig. 5 we show the calculated phonon DOS for the rocksalt and wurtzite phases along with the observed spectrum for a pressure of 51 GPa. The observed Raman spectrum is clearly due to disorder activated scattering from the phonons of the rocksalt structure. We have included in Fig 2 the Raman features R_1, R_2, and R_3 which have their origins in disorder activated scattering from LA (R_1) and the X and L points (R_2 and R_3, respectively) of the LO branch phonons of the rocksalt phase. Also on the figure are the predicted shifts in the zone centre phonon modes of the wurtzite phase and the dependence of the corresponding positions in the rocksalt phonon DOS for the R_1, R_2, and R_3 lines with pressure above 45 GPa. The disorder activation of the Raman scattering from the phonon density states in a semiconductor after a high-pressure phase transition has been observed before in recovered material [for example, GaAs (Ref. 15)]. Here we demonstrate the use of such a spectrum to study the transition itself.

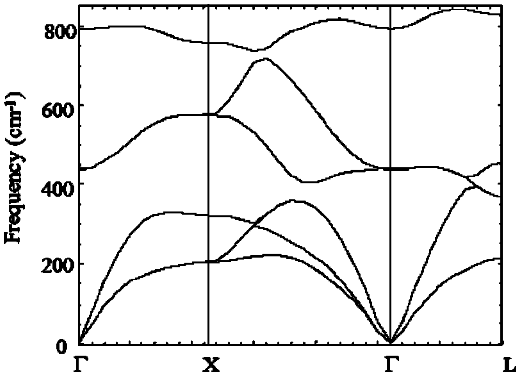

FIG. 4. Calculated phonon dispersion curves for GaN in the rocksalt structure at 50 GPa.

The wurtzite to rocksalt phase transition was recently predicted[11] by calculations based on the LDA to proceed via an orthorhombic path (the orthorhombic structure being a common subgroup of the two structures). The phase transition occurs in this case by compression along the wurtzite

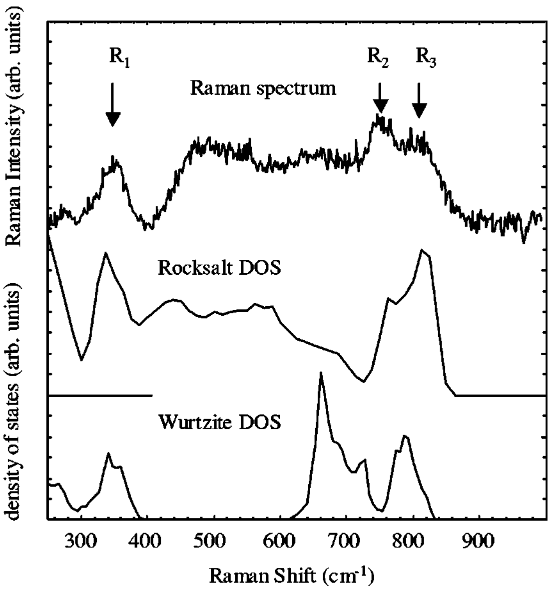

FIG. 5. Comparison between the calculated phonon density of states for GaN at 50 GPa and the observed Raman spectrum. The Raman Feature R_1, R_2, and R_3 are due to scattering from the LA, LO (X point), and LO (L point) peaks in the density of states of the rocksalt phase. The evolution of these feautures with pressure is included in Fig. 2 along with their calculated pressure dependence.

c-axis followed/accompanied by a compression along one of the wurtzite three fold [0100] axes to form the rocksalt [100] axes. One of the fundamental aspects of the phase transition in general is the large reduction in volume that occurs (7%). Clearly in this model there is an arbitariness about the resulting relationship between the initial wurtzite *a/b* plane crystallographic axes and the final rocksalt ones. We should therefore expect a high degree of disorder in the resulting (001) plane (where the [001] axis corresponds to the original wurtzite *c*-axis). The Raman results cannot directly confirm any transition pathway, however, we observe that the rocksalt structure spectrum shows strong scattering in the spectral region 600–700 cm^{-1}. This corresponds to a minimum (not zero) in the calculated phonon density states. The phonons giving rise to this scattering have wave vectors in the region (extending over a range of *k*-vectors) of the *K* point on the $\Gamma-\Sigma-X$ axis of the brillouin zone. There appears to be no reason for this on the grounds of point group symmetry. It would be expected, however, of the symmetry was lowered along this axis by high level of disorder along the (110) axis such as would occur if nanocrystals bounded by [110] planes (the natural cleavage planes of the cubic structure) were formed during the phase transition.

As discussed in the above, an intermediate layer MgO-*h* phase has been suggested in this system.[11] This phase is predicted to form by during an initial compression of the wurtzite along the *c*-axis to from a structure, which is isomorphic to the hexagonal boron nitride structure. This structure is symmetrically almost identical to wurtzite with the addition of an extra mirror plane. Crucially the material is predicted to be semimetallic with a band gap close to zero. We should expect the phonon structure to be similar for this phase with the same number of modes of each symmetry, (the frequencies will change substantial) and in particular the LDA calculation predicts a large acousto-optic gap in the phonon density of states. It is clear from Fig. 3 that we observe a smooth evolution of the spectra from the phonon lines of the wurtzite structure to the disorder induced scattering from the rocksalt phase phonons. This suggests that the transition occurs instantaneously on a local scale, resulting in the very high degree of local disorder. If an initial compression were to occur along the *c*-axis of the wurtzite structure then hexagonal symmetry would be conserved and we would expect much less disorder in the resulting MgO-*h* structure. This would show up as strong shifts in all the Raman scattering from zone centre phonons in the region of the transition pressure preceding the appearance of the rocksalt disordered scattering. This is not observed; thus, there is no evidence for an intermediate phase in our data.

Finally, absorption measurements were performed by simply focussing white light onto the bottom of the sample and recording the transmitted spectrum. Figure 6 shows the resulting spectrum at 61 GPa, in the figure the known sample thickness is used to calculate the value of the absorption coefficient for rocksalt GaN in cm^{-1}. The figure is then plotted with vertical scale of log of the absorption coefficient. The measured shift in the absorption feature with pressure is $dE/dP \approx 18\ \text{meV/GPa}$. The absorption edge tail is approximately exponential with photon energy and is not well fitted by either a quadratic or square root dependence. It is thus not consistent with purely indirect or direct transitions between bands in a semiconductor but with absorption by defect states below a band edge. Our LDA calculations indicate an indirect gap in the visible part of the spectrum for rocksalt GaN in agreement with those of Ref. 8. The magnitude of the predicted indirect gap is 2.2 eV at 61 GPa and that of the direct gap is 5.4 eV at the same pressure. However, the observed absorption feature occurs between 1.6 and 1.7 eV. It is well known that LDA calculation underestimate band gaps due to quasiparticle self-energy corrections. We observe that our estimate of the unpressurised wurtzite GaN band gap is 2.4 eV, smaller than the experimental value by 1 eV but in line with other workers calculations for the wurtzite case. In Ref. 8 they estimate an unpressurized gap of 1.69 eV for the rocksalt structure, still too large to be consistent with the feature we observe in the absorption spectrum. Moreover, the absolute value of the absorption coefficient is much higher than is generally observed for an indirect transition. We have already demonstrated that the poor long range order in the lattice results in the breaking of *k*-selection rules in the Raman scattering, it is likely to strongly affect the absorption as well. We suggest that the observed feature is due to disorder induced states in the actual rocksalt phase energy gap. Although further experiments would be needed to confirm this, it should be noted that we observe that the recovered GaN also displays a below band edge absorption feature as a result of such defects. What is clear is that the GaN material in this experiment remains a semiconductor with band gap greater than 1.5 eV throughout the phase transition range and there is no evidence for the predicted semimetallic behavior. We also conclude that the previously reported [9] opacity of rocksalt GaN in poorer quality bulk samples was due to a similar process.

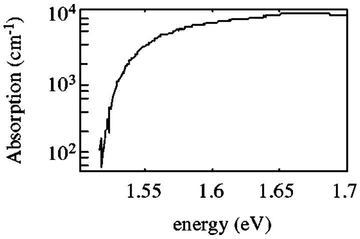

FIG. 6. Absorption spectra of rocksalt phase GaN at 61 GPa.

In summary we have presented a careful optical (Raman scattering and absorption) study of the wurtzite to rocksalt high pressure structural phase transition in high quality epitaxially grown GaN. During the phase transition both the Raman and absorption spectra of the wurtzite phase smoothly evolve into those of the disorder activated raman scattering from the phonons of the rocksalt phase with no evidence for an intermediate phase. Absorption measurements show an absorption feature at 1.6 eV at a pressure of 61 GPa.

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