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In this communication, the impact of precursor pyrolysis temperature on the Raman spectroscopic properties of nanphase GaN derived from the polymeric gallium imide $\{Ga(NH)_{3/2}\}_n$ is reported. GaN prepared by pyrolysis at either 900 or 1100 °C exhibit modes at approx. 570 and 730 cm^{-1} consistent with the presence of hexagonal GaN. Employing a lower conversion temperature of 700 °C produces a lattice with extensive defects, as evidenced by the prescence of additional bands at 332, 410, 637, and 744 cm^{-1}; additional heating of this type of sample at 900 and 1000 °C diminishes the intensity of these defect-related modes. Raman spectra of nanophase aluminum nitride (AlN) and an aluminum gallium nitride (AlGaN) composite prepared from pyrolysis of the requisite precursors at a fixed temperature of 900 °C are also presented.

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MICRO-RAMAN INVESTIGATION OF NANOCRYSTALLINE GaN, AlN, and an AlGaN COMPOSITE PREPARED FROM PYROLYSIS OF METAL AMIDE-IMIDE PRECURSORS

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Abstract

In this communication the impact of precursor pyrolysis temperature on the Raman spectroscopic properties of nanophase GaN derived from the polymeric gallium imide $\{Ga(NH)_{3/2}\}_n$ is reported. GaN prepared by pyrolysis at either 900 or 1100°C exhibit modes at approx 570 and 730 cm^{-1} consistent with the presence of hexagonal GaN. Employing a lower conversion temperature of 700°C produces a lattice with extensive defects as evidenced by the presence of additional bands at 332, 410, 637, and 744 cm^{-1}; additional heating of this type of sample at 900 or 1000°C diminishes the intensity of these defect-related modes. Raman spectra of nanophase aluminum nitride (AlN) and an aluminum gallium nitride (AlGaN) composite prepared from pyrolysis of the requisite precursors at a fixed temperature of 900°C are also presented.

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Extensive research regarding Group III nitride semiconductors continues at a dizzying pace, motivated to a large extent by the development of new blue and green light emitting diodes and lasers in pragmatic opto-electronic devices.[1] As a part of these efforts, new synthetic routes for the formation of bulk nanocrystalline gallium nitride and related aluminum gallium nitride alloys have recently been reported, with specific variations in the pyrolysis conditions enabling some control over the particle nanosize and a degree of crystalline phase-inhomogeneity of the materials.[2] Recent collaborative efforts from our laboratories have particularly examined the impact of precursor chemistry and specific preparative conditions on the luminescence of the resultant nanophase GaN and related alloys which can be formed;[3] such measurements are useful in assessing the presence of defect or non-radiative sites in the solid(s). While photoluminescence, electron microscopy, and x-ray diffraction techniques are all useful characterization methods of these materials, Raman spectroscopy has been shown to be a unique structural probe of lattice vibrations in metal nitride thin films and single crystals.[4] Thus we report in this communication the impact of precursor pyrolysis temperature on the Raman spectroscopic properties of nanophase GaN derived from the polymeric gallium imide, $\{Ga(NH)_{3/2}\}_n$. We also examine the Raman spectra of nanophase aluminum nitride (AlN) and an aluminum gallium nitride composite prepared from pyrolysis of the requisite precursors at a fixed temperature (900°C).

The preparation of the polymeric gallium imide, $\{Ga(NH)_{3/2}\}_n$, was accomplished according to the published method.[2b] This precursor was pyrolyzed to nanophase GaN at either 700, 900, or 1100°C under an ammonia flow as previously described.[3b] The analyses by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM) of the solid products were consistent with the formation of nanocrystalline GaN existing as a mixture of cubic and hexagonal phases after heating at 700°C (or below) but being prevailingly hexagonal after heating at 900 or 1100°C.[2b,3] Nanocrystalline AlN was prepared from pyrolysis at 900°C of an Al-amide-imide precursor synthesized from the reaction of $[Al(NMe_2)_3]_2$ with NH_3.[3b] A mixed aluminum gallium nitride nanocomposite was prepared in an analogous fashion by the 900°C pyrolysis of a mixed aluminum/gallium amide-imide precursor synthesized from transamination/deamination reactions in the bimetallic system $[M(NMe_2)_3]_2/NH_3$ (M = Al/Ga =1/1; precursor 4 in reference 3b).[3b] GaN samples prepared by pyrolysis at 700°C were subsequently heat treated in a quartz cell for 30 minutes in a nitrogen atmosphere at 900°C, followed by subsequent heating of this sample at 1100°C. Heating and cooling rates of 5 degrees/min were employed.

Raman spectra were obtained by illuminating the sample with the 514 nm line of an Ar^+ laser. The laser beam was focused by a 100x objective of a confocal microscope (Olympus BH2) and Raman spectra were obtained from a 0.5 μm diameter spot size. The backscattered light was collected by the same objective and the spectral analysis was done using an axial transmissive spectrograph (Kaiser Optical Systems, HoloSpec) equipped with a Princeton Instruments CCD camera. Spectra of the metal nitride nanocrystallites in the frequency range between 200 cm^{-1} and 1700 cm^{-1} were obtained using a 30 second integration time. Raman measurements were conducted at room temperature. In order to improve the signal to noise ratio, the nanocrystalline powders were pressed into a 2 mm groove in a stainless steel plate. A hydrostatic pressure of about 1 MPa was applied for approximately 2 minutes. The compressed sample had a smooth surface that reduced scattering in random directions and increased the intensity of the backscattered light. The sample holders were then placed on the horizontal surface of the computer controlled x-y-z positioning stage (Oriel, Encoder Mike), which was attached to the microscope. Raman spectra of five different spots of the sample surface were recorded. Each measurement was reproduced one to three times; no changes in the band shapes were observed, indicating that the samples were uniform (at least on a scale greater than 0.5 micrometer).

The Raman spectrum of nanocrystalline GaN (average diameter ~ 21 nm) prepared by pyrolysis of a gallium imide precursor at 900°C is illustrated in Figure 1 for the range 400-1000 $cm.^{-1}$ Two features are clearly evident. The most intense peak, at 570 cm^{-1}, is the well-known mode of E_2 symmetry for hexagonal GaN.[4] A weaker band at 730 cm^{-1} is also seen, assigned to the LO phonon of A_1 symmetry for hexagonal GaN.[4] Examination of different grains of this material in micro-Raman mode reveal only minor variations in the ratio of intensities of the E_2 to A_1(LO) peaks. Cubic GaN exhibits a very similar Raman spectrum to the hexagonal phase (cubic TO phonon at 555 cm^{-1}, LO phonon at 740 cm^{-1}).[4b] Previous X-ray powder diffraction studies of this type of GaN nanoparticles have determined that both cubic and hexagonal phases of GaN exist in products obtained from pyrolyses of the precursor up to 700°C, while the hexagonal phase appears to dominate at higher conversion temperatures.[2b,3] Our Raman data are consistent with the dominant hexagonal phase of GaN in this sample, in agreement with previous XRD observations.[3b]

Nanocrystalline GaN prepared by pyrolysis at the higher temperature of 1100°C reveals a comparable Raman spectrum in terms of number of bands and their location; however, there is an appreciable increase in the intensity of the A_1 phonon (720 cm^{-1}) relative to the E_2 mode (570 cm^{-1}). Given (1) previous reports citing the strong polarization dependence of the relative intensities of these modes in epitaxially-grown GaN thin films[4a,b] and (2) the obvious random orientation of these nanocrystals, we do not ascribe any significance to this variation in the ratio of E_2 to A_1 intensities. However it is clear that for both of these conversion temperatures, the observed Raman spectra are strong evidence for crystalline GaN and consistent with hexagonal as the dominant phase of this material.

Interestingly, employing the lower pyrolysis temperature of 700°C for the conversion of the gallium imide precursor to GaN results in a radically-different Raman spectrum (Figure 2). This material exhibits a Raman spectrum with intense peaks at 332, 410, 637, and 744 $cm.^{-1}$ A weak shoulder at 722 cm^{-1} is also observed, presumed to be the A_1 (LO) mode of hexagonal GaN. These intense modes, not observed in the GaN nanocrystals grown at higher temperatures, are very similar to bands previously reported for epitaxially-grown GaN layers subjected to extensive ion implantation with Ar^+, Mg^+, P^+, C^+, and Ca^+.[4c] In this previous study, it was determined that the intensity of Raman modes appearing at 360, 420, and 670 cm^{-1} are directly proportional to ion dose, and independent of the choice of ion.[4c] These Raman active features have been attributed to damage of the lattice by ion bombardment.[4c] The origin of the observed mode at 744 cm^{-1} is not clear at present. Based on the existing literature it is possible that it is (1) the normally very weak E_1 mode for hexagonal GaN[4b] or alternatively (2) a mixed E_1 (LO) / A_1 mode (described as a "quasi-LO phonon")[4e] in principle observable upon using narrow aperatures of the focusing lens in micro-Raman measurements. For a perfect, infinite crystal, Raman scattering occurs only the center of the Brillouin zone. The selection rule $\Delta \mathbf{k} = 0$ is not valid for small crystals or crystals with extensive defects, and other points from the Brillouin zone can contribute to the spectrum. For the nanocrystalline GaN studied here, it is reasonable to assume that at the appreciable lower conversion temperature of 700°C extensive lattice defects remain, possibly induced by residual fragments of dimethylamino groups and/or hydrogen of the precursor. These additional Raman modes are attributed to lattice defects rather than formation of some type of amorphous phase since previous x-ray diffraction and transmission electron microscopy studies of this material have established that it is indeed nanocrystalline GaN.[2b,3] In principle, it is also possible to interpret these additional modes as second order Raman scattering from hexagonal GaN, similar to the recent observations of Siegle et al.[5] However, given the nature of our preparative method and the fact that second order Raman features are typically very weak in their intensity, we tend to believe that the observed features in this particular sample type are defect-related.

In order to confirm this hypothesis, we next examined the effect of additional heating of these GaN samples initially prepared by pyrolysis at 700°C. After heating in a quartz cell for 30 minutes in a nitrogen atmosphere at 900°C, the modes at at 332 and 744 cm^{-1} disappear, and the intensity of the 410 cm^{-1} band is greatly diminished. The dominant spectral features are now the 565 and 730 cm^{-1} E_2 and A_1 modes of crystalline GaN (Figure 2). Heating this same sample at the slightly higher temperature of 1100°C results in similar behavior, i.e the defect-related modes are substantially diminished in their intensity and the E_2 and A_1 vibrational modes of GaN dominate the observed Raman spectrum.

The Raman spectrum of nanocrystalline AlN prepared by the pyrolysis at 900°C of an Al-amide-imide precursor is shown in Figure 3. An intense feature at 657 cm^{-1} is observed, consistent with the previous reports as the phonon of E_2 symmetry for hexagonal AlN. We do not observe the weak TO phonons of A_1 and E_1 symmetry at 610 and 670 cm^{-1}, respectively. This observation is not surprising given the strong angular dependence demonstrated for these modes in AlN films on sapphire.[4a] For an aluminum gallium nitride nanocomposite prepared by pyrolysis at 900°C, modes at 538 cm^{-1} (weak shoulder) and 567 cm^{-1} (strong) are observed. Previous studies of $Al_xGa_{1-x}N$ films have shown that the off-resonance Raman spectrum is often dominated by the intense E_2 mode,[4c-4f] and our observations are consistent with these results.

Summary

We have demonstrated that micro-Raman spectroscopy is a useful tool for the characterization of nanocrystalline Group III semiconducting nitride powders and a qualitative probe of the presence of lattice defects in these solids. The defects can be removed by subsequent heating at temperatures of 900°C or higher. Such studies reinforce the necessity of using relatively high temperatures in the formation of GaN from polymeric single source precursors in order to eliminate such defects. Further studies evaluating other types of metal nitride precursors and the role of reaction conditions on structure in these materials are planned.

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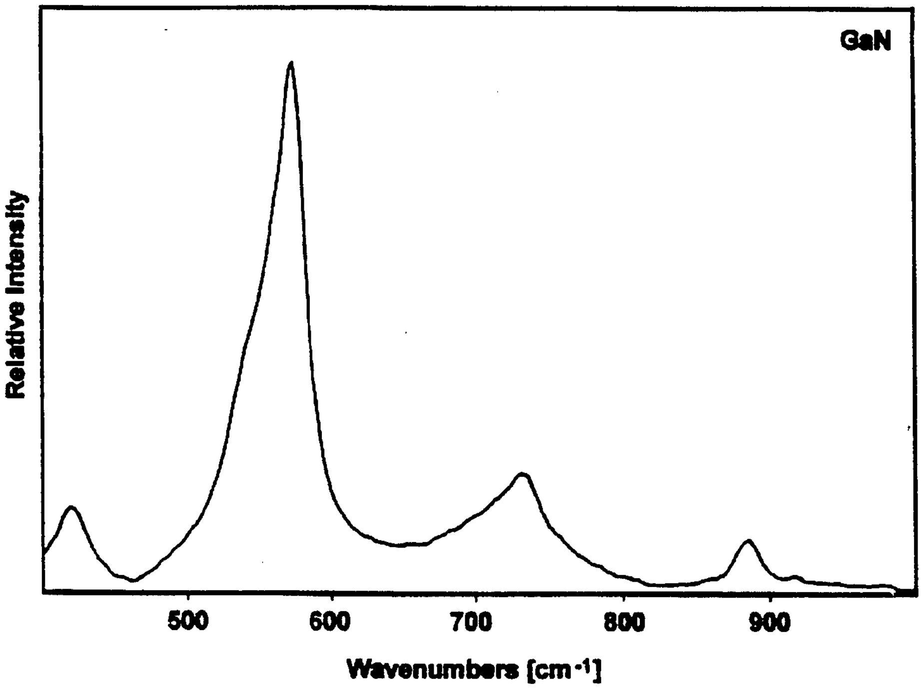
Figure Captions.

Figure 1. Room temperature Raman spectrum of GaN nanocrystals prepared from pyrolysis of a gallium imide precursor at 900°C in an ammonia atmosphere. The observed band at 570 cm^{-1} corresponds to an E_2 mode, while the 730 cm^{-1} feature is attributed to a LO phonon of A_1 symmetry. Spectra were obtained by illuminating the sample with the 514 nm line of an Ar^+ laser in a backscattering geometry.

Figure 2. (a) Room temperature Raman spectrum of GaN nanocrystals initially prepared from pyrolysis of a gallium imide precursor at 700°C in an ammonia atmosphere. (b) Effect of additional heating of this sample at a temperature of 900°C for 30 minutes in a nitrogen atmosphere; (c) Effect of additional heating of this sample at a temperature of 1100°C for 30 minutes in a nitrogen atmosphere. Spectra were obtained by illuminating the sample with the 514 nm line of an Ar^+ laser in a backscattering geometry.

Figure 3. (a) Room temperature Raman spectrum of AlN nanocrystals prepared from pyrolysis of an aluminum amide-imide precursor at 900°C in an ammonia atmosphere; (b) Room temperature Raman spectrum of AlGaN nanocomposite prepared from pyrolysis of a mixed gallium/aluminum imide precursor at 900°C in an ammonia atmosphere. Spectra were obtained by illuminating the sample with the 514 nm line of an Ar^+ laser in a backscattering geometry.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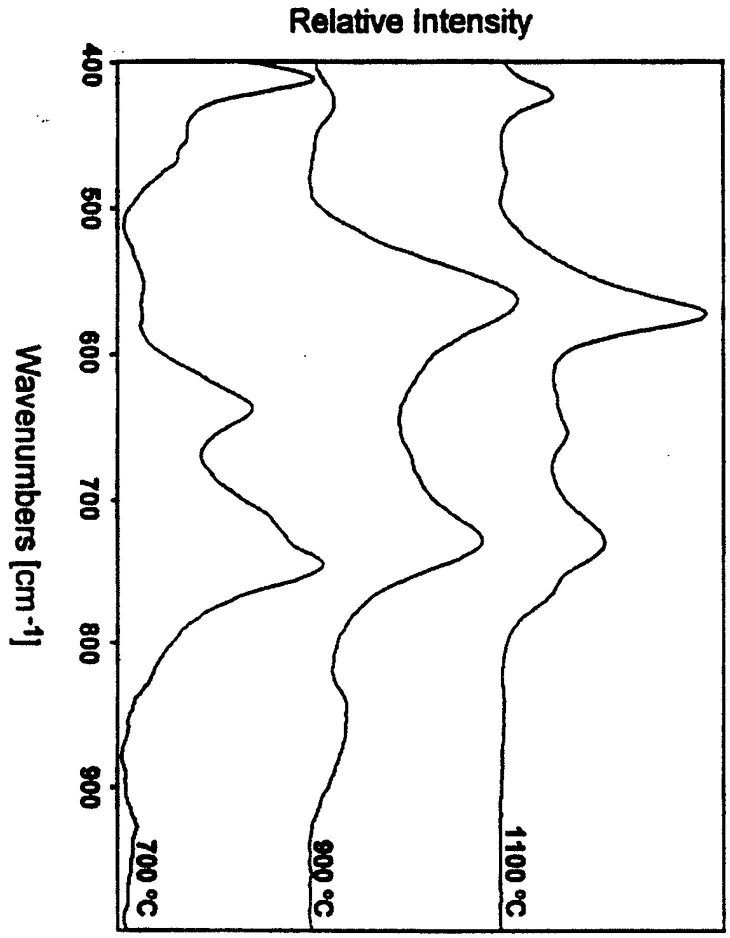
700
800
900
Wavenumbers [cm⁻¹]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Wavenumbers [cm-1]
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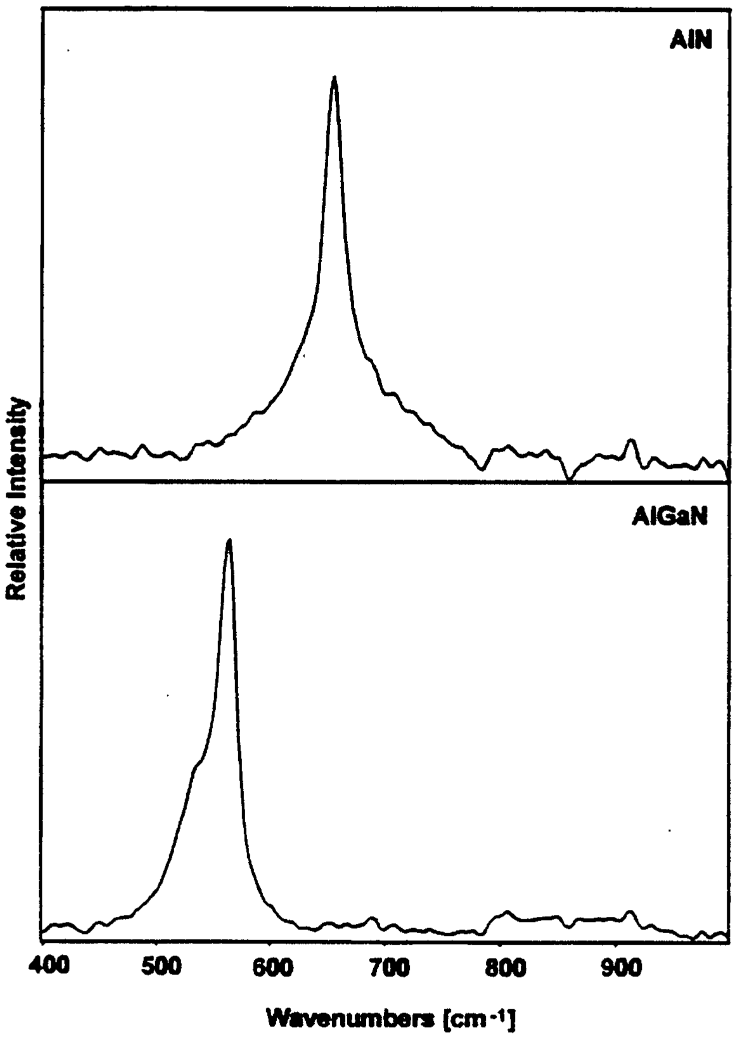
600
700
800
900
700 °C
900 °C
1100 °C


AlN
AlGaN
Relative Intensity
400
500
600
700
800
900
Wavenumbers [cm⁻¹]

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