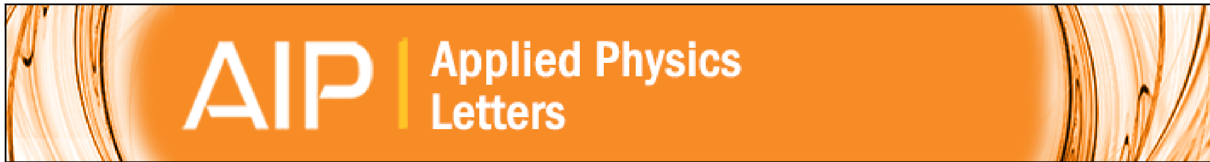

Local structures of free-standing Al x Ga 1−x N thin films studied by extended x-ray absorption fine structure

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Local structures of free-standing $Al_xGa_{1-x}N$ thin films studied by extended x-ray absorption fine structure

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Local structural information for the first two atomic shells surrounding Ga atoms in free standing $Al_xGa_{1-x}N$ alloy films has been obtained by extended x-ray absorption fine structure spectroscopy. For an AlN mole fraction ranging from 0 to 0.6, we found that the first shell Ga–N bond length had only a weak composition dependence, roughly one quarter of that predicted by Vegard's Law. In the second shell, the Ga–Ga bond length was significantly longer than that of Ga–Al ($\Delta \sim 0.04-0.065$ Å). A bond-type specific composition dependence was observed for the second shell cation–cation distances. While the composition dependence of the Ga–Ga bond length is ~70% of that predicted by Vegard's Law, the Ga–Al bond length was essentially composition independent. These results suggested that local strain in $Al_xGa_{1-x}N$ was also accommodated by lattice distortion in the Al cation sublattice. © *1999 American Institute of Physics.* [S0003-6951(99)03852-8]

Group III nitrides and their ternary alloys have attracted much attention in recent years because of the potential for utilization in light emitting devices in the green to ultraviolet (UV) range of the spectrum.[1–3] However, despite many investigations on the electrical, optical, and microstructural properties on these materials, little information has been reported on the local atomic structure of these alloys.

Structural models on ternary III–V and II–VI semiconductor alloys have been developed in the last two decades largely based on information obtained from extended x-ray absorption fine structure (EXAFS) measurements.[4–11] Recently, a few EXAFS studies on ternary III nitrides have also been reported.[12–16] In particular, Ga K edge EXAFS experiments performed by Miyano *et al.*[15] on $Al_xGa_{1-x}N$ with AlN mole fractions ranging from 0 to 0.44, showed that the Ga and Al atoms were randomly distributed in the alloy with Ga–N bond lengths close to that of GaN. However, previous EXAFS studies on $Al_xGa_{1-x}N$ were restricted to a photoelectron momentum (k) range of $\leq 10-12$ Å^{-1} due to technical limitations. (The work by Miyano *et al.*[15] was performed with a k range up to 14 Å^{-1}.) Furthermore, the alloy composition was not measured independently, but was normally estimated from the growth conditions. Consequently, the accurate determination of the local structural parameters of the nearest neighbors was severely limited.

In this article, we report an EXAFS investigation on AlGaN thin films with AlN mole fraction ranging from 0 to 0.6. We have utilized a laser lift-off (LLO) technique to separate the sapphire substrate from the alloy thin films and as a consequence, the EXAFS experiments were performed to $k = 20$ Å^{-1} without contamination due to diffraction from the substrate. In addition, the growth stress associated with the thermal expansion mismatch with the sapphire substrate was relieved by lift-off. Our measurements were also performed at cryogenic temperatures to minimize signal damping due to thermal vibration and thus, enhance contributions from the second nearest neighbors. Furthermore, alloy compositions of the films were accurately measured by Rutherford backscattering spectrometry (RBS) and independently confirmed by optical absorption measurements.[17]

The $Al_xGa_{1-x}N$ thin films (0.3–1.4 μm thick) were grown on (0001) sapphire substrates by metal organic chemical vapor deposition (MOCVD). Laser lift-off of GaN thin films from sapphire substrates, without degradation of the film quality, has been demonstrated recently by using the irradiation from a KrF pulsed excimer laser (248 nm) directed through the transparent sapphire substrate to separate GaN thin films from sapphire substrates.[18] The same LLO process was performed to prepare the samples reported in this letter. The laser irradiation induces the decomposition of the $Al_xGa_{1-x}N$ $(0<x<0.6)$ at the substrate-thin film interface. Separation of the sapphire from the $Al_xGa_{1-x}N$ film was then completed by melting the thin Ga rich interfacial layer ($T_m = 30$ °C). The free-standing $Al_xGa_{1-x}N$ films were supported and encapsulated in Kapton tape.

EXAFS measurements were carried out at 20 K on

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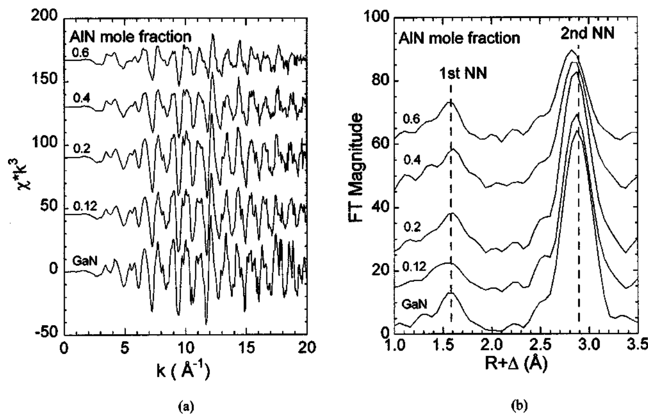

FIG. 1. (a) k^3-weighted, isolated Ga *K*-edge EXAFS oscillations from $Al_xGa_{1-x}N$ samples with $x=0-0.6$ and (b) nonphase-corrected Fourier transform magnitudes of the EXAFS spectra over a *k* range of 2–19 Å^{-1}.

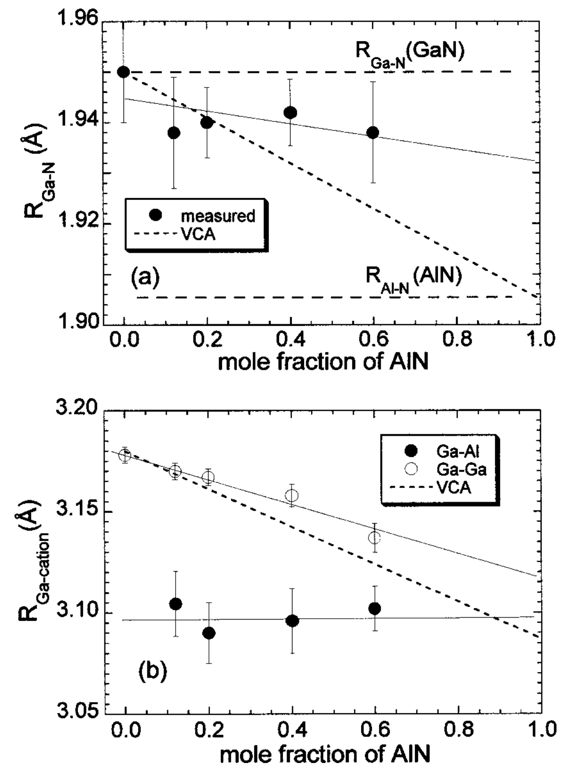

FIG. 2. (a) Ga–N nearest neighbor bond lengths and (b) Ga-cation (Ga/Al) second nearest neighbor bond lengths for $Al_xGa_{1-x}N$ samples with $x=0-0.6$. Bond lengths calculated using the virtual crystal approximation are also shown.

beamline 4-3 at the Stanford Synchrotron Radiation Laboratory. The Ga K_α fluorescence signals from the alloy samples were collected by a 13-element Ge x-ray spectrometer. The raw EXAFS data were analyzed by the SPLINE and XFIT code[19] using backscattering amplitudes and phase shifts determined from *ab initio* calculations (FEFF4.0).[20]

Figure 1(a) shows the k^3-weighted Ga *K*-edge EXAFS oscillations, isolated from the fluorescence spectra, of the $Al_xGa_{1-x}N$ samples with $x=0$ to 0.6. Note that the noise level was much lower than the oscillation amplitude for all the spectra for $k \leqslant 20$ Å^{-1}. The corresponding Fourier transformation (FT) magnitudes for a *k* range of 2–19 Å^{-1}, are shown in Fig. 1(b). The EXAFS spectra showed a monotonic decrease in amplitude as the AlN mole fraction and thus, the second nearest neighbor (NN) Ga–Al coordination, increased.

No noticeable change in the position of the first NN Ga–N was apparent in the FT magnitude shown in Fig. 1(b). The Ga–Al and Ga–Ga bonds that comprised the second NN peak were not resolvable and thus, yielded but a single peak. However, a significant monotonic shift to lesser distances was observed due to the lesser Ga–Al bond length relative to that of Ga–Ga. The decrease in FT magnitude of the second NN peak, as well as the overall EXAFS amplitude, with increasing AlN mole fraction arises from the reduced scattering amplitude of Al and the interference of the scattering waves from the Ga and Al atoms at similar distances from the absorbing Ga atoms in the ternary alloys. Such reduction in the EXAFS and FT amplitudes can also be attributed to the increase in the Debye–Waller factor (the relative mean square deviation in bond length, σ^2) for the Ga–Al (from 0.0002 to 0.002 Å^2) and Ga–Ga (from 0.0018 to 0.0027 Å^2) second NN bonds as a function of AlN mole fraction.

Structural parameters of the first and second NN shells were determined by inverse transforming the FT spectra over a *R* range of 1.0 to 3.2 Å. Figure 2(a) shows the experimental values of the Ga–N bond lengths, R_{Ga-N} as a function of the AlN mole fraction. The R_{Ga-N} and R_{Al-N} for crystalline GaN and AlN, respectively together with the calculated R_{Ga-N} for $Al_xGa_{1-x}N$ in the virtual crystal approximation (VCA) are also shown for comparison. The solid line was a linear fit to the experimental data. The VCA is an extrapolation of Vegard's law assuming a linear dependence of bond length on composition.[8,21] It is obvious from the figure that the R_{Ga-N} had only a weak dependence on composition, approximately one quarter of that predicted by the VCA dependence and was thus closer to the Bragg–Pauling composition-independent limit[22,23] than the Vegard limit.[20] Both the values and the composition dependence of the R_{Ga-N} were consistent with those reported by Miyano *et al.*[15] for $Al_xGa_{1-x}N$ and in general, with the first NN bond length distortion observed in other III–V alloys.[3,4] The weak compositional dependence of R_{Ga-N} suggested that local strain was accommodated by bond angle changes rather than bond length distortion.

The second NN Ga–Al and Ga–Ga bond lengths (R_{Ga-Al} and R_{Ga-Ga}, respectively) shown in Fig. 2(b) differed significantly from those observed in other ternary III–V[4,5] and II–VI[6,7] semiconductor systems. The two Ga-cation distances were dissimilar, especially for low AlN mole fraction where $R_{Ga-Ga}-R_{Ga-Al}=0.065$ Å for $x=0.12$, with different composition dependencies. R_{Ga-Ga} had a much greater composition dependence than the first shell R_{Ga-N} though less than that predicted by the VCA ($\Delta R_{Ga-Ga}/\Delta x = -0.065$, $\Delta R_{Ga-Ga}(\mathrm{VCA})/\Delta x=-0.093$). Conversely, R_{Ga-Al} was essentially composition independent. This differed from the cation–cation distances in other III–V alloys. For example, with InGaAs, Mikkelsen and Boyce[5] found that the second NN cation–cation distances, R_{Ga-Ga}, R_{Ga-In}, and R_{In-In} were within 0.08 Å and all followed the same $R_{cation-cation}$ composition dependence calculated using the VCA. For the $Al_xGa_{1-x}N$ alloys in this article, we found that the second NN cation–cation distance exhibited a bond-type specific composition dependence. Similar dependencies were

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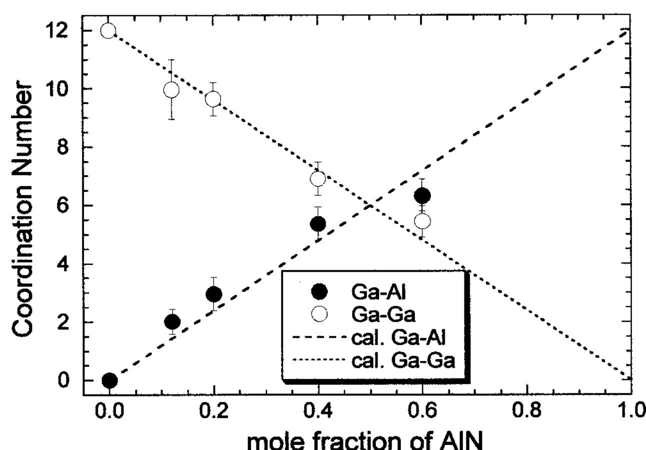

FIG. 3. The second shell Ga–Ga and Ga–Al coordination numbers for the $Al_xGa_{1-x}N$ samples with $x=0-0.6$. Coordination numbers calculated assuming a random alloy are also shown.

not seen in III–V and II–VI ternary alloys, but were reported recently for the first NN bond lengths in Si_xGe_{1-x} alloys.[24,25] Aubry *et al.*[24] showed that the extent of Pauling behavior of the first NN distance in Si_xGe_{1-x} alloys depended on the bond type (Si–Si, Si–Ge, or Ge–Ge) and suggested that differences in the pairwise electronic interactions may influence the bond length-composition trend. A similar bond-type dependence was also reported by Ridgway *et al.*[25] in both crystalline and amorphous SiGe alloys.

Differences in bond length and composition dependences for Ga–Al and Ga–Ga second NN distances were not observed previously in $Al_xGa_{1-x}N$ alloys by Miyano *et al.*[15] These authors reported that R_{Ga-Al} was less than R_{Ga-Ga} by ~0.02 Å and both of them closely followed the composition dependence predicted by the VCA. However, given the smaller composition and ranges measured by Miyano *et al.* and the magnitude of the resulting error (for example, ±0.06 Å for R_{Ga-Al}), these results should be treated with caution. Furthermore, the presence of sapphire substrate during the EXAFS measurements could have been an additional source of strain that could modify the structural parameters of the alloy films reported by these authors.

Finally, Fig. 3 shows the second shell coordination number (CN) for both the Ga–Ga and Ga–Al pairs. The CN agreed with that calculated by assuming a random site occupancy of Al in the cation sublattice. This confirmed that no alloy ordering or clustering was present in the samples and therefore, the structural parameters were representative of random $Al_xGa_{1-x}N$ alloys.

In conclusion, the structural parameters of the first two atomic shells surrounding Ga atoms in free-standing $Al_xGa_{1-x}N$ films with x ranging from 0 to 0.6 were measured by EXAFS. Compared with previous experiments, greater ranges of composition and photoelectron momentum were examined. For the first NN shell, R_{Ga-N} was closer to the Bragg–Pauling than Vegard limit and decreased only slightly with x. The second NN Ga–Ga bond length was significantly larger than that of Ga–Al ($R=0.065$ Å for $x=0.12$) and different compositional dependencies were observed for R_{Ga-Ga} and R_{Ga-Al}. R_{Ga-Ga} had a much greater composition dependence than the first shell R_{Ga-N} though only ~70% of that was predicted by the VCA. In contrast, R_{Ga-Al} was essentially composition independent. These results suggested that local strain in $Al_xGa_{1-x}N$ alloys was also accommodated by lattice distortion in the Al cation sublattice.

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