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Complex and incommensurate ordering in $Al_{0.72}Ga_{0.28}N$ thin films grown by plasma-assisted molecular beam epitaxy

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Structures with incommensurate ordering along the [0001] direction are observed in wurtzite $Al_{0.72}Ga_{0.28}N$ alloys grown by plasma-assisted molecular beam epitaxy on *c*-plane sapphire. Films grown in environments with group-III/N ratios greater than 1 exhibit ordered superlattice structures that are incommensurate with the wurtzite crystal lattice. In contrast, films grown under nitrogen-rich conditions exhibit ordered structures with a periodicity of four cation-N monolayers. The increasing complexity of the ordering with increasing Ga-rich growth environment suggests that the ordering is related to the presence of a Ga overlayer believed to exist on the surface of the growing film. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2201898]

Wurtzite III–V nitride semiconductors have applications in electronic, optoelectronic, and electromechanical devices. Chemical ordering along the *c* axis in $Al_xGa_{1-x}N$ films has been reported in a number of previous studies,[1–11] and may have important consequences for the transport properties of the material.[12] Recent annealing studies of $Al_xGa_{1-x}N$ films have suggested that the ordered state is not the equilibrium state.[13] Indeed, since diffusion in the bulk at ambient temperatures is quite slow it is believed that ordering occurs at the surface during growth, as for the arsenides and phosphides.[14] However, the ordering mechanisms at the surfaces of wurtzite III-V nitrides are apparently quite different than is the case for the cubic arsenides and phosphides. The first observations of ordering in these materials were of simple alternating Ga-rich and Al-rich (0001) layers in $Al_xGa_{1-x}N$.[1] Northrup and Neugebauer[15] suggested that ordering could arise from preferential incorporation of Al and Ga at alternating nonequivalent step-edge sites. However, Iliopoulos *et al.*[4] and Ruterana *et al.*[5] have shown complex 12 ML (monolayer) ordering with coexistence of different ordering types; these cannot easily be explained by the step-edge growth mechanism.

Here we report an incommensurate ordering which depends on the group-III/N atomic flux ratio present during growth by plasma-assisted molecular beam epitaxy (PA-MBE). Theoretical understanding of how these ordered structures arise during thin film growth is unclear, but the dependence of this ordering on growth conditions suggests that it must be intimately related to the unusual nature of the Ga-rich surface during growth.[16] Iliopoulos *et al.*[17] have reported that the kinetics of $Al_xGa_{1-x}N$ growth by MBE is fundamentally different from the kinetics of $Al_xGa_{1-x}As$ growth. They attributed this to the difference in Al–N and Ga–N bond strengths versus the closely similar Al–As and Ga–As bond strengths. For the group-III nitrides, Al incorporates with high probability in both group-III and N-rich growth regimes. Thus, Iliopoulos *et al.* suggested that the incorporation of Ga is controlled solely by the available N flux that is not consumed by Al atoms. As a result, the Ga flux can be increased significantly without affecting the Al mole fraction of the films. The excess Ga is believed to form a thin overlayer on the surface during growth.[16] The steady-state thickness of this layer is determined by the Ga arrival, incorporation, and evaporation rates, the latter being strongly dependent on the substrate temperature. Although the Ga overlayer on the surface does not incorporate and hence does not alter the alloy composition, the presence and thickness of this Ga film must play an important role in the structural, electronic, and optical properties of the final AlGaN alloy.

In this study, a series of AlGaN alloy films was deposited onto *c*-plane sapphire by PA-MBE using different group-III/N ratios. The samples were grown using a three-step method. The substrate was first nitridated by exposure to nitrogen plasma at 870 °C. An AlN buffer layer was then deposited at the same temperature, followed by growth at temperatures of 750–800 °C. Four samples were grown, each with final composition of approximately 72% Al, using different conditions of group-III/N ratio and Si doping levels. Samples A and B were grown under similar conditions in an environment having a group-III/N ratio close to 1. However, sample B was doped heavily *n* type with Si. Sample C was grown under group-III-rich conditions with a Ga flux that was approximately 20% higher than for samples A and B. Sample D was grown under N-rich conditions with Ga and Al fluxes reduced by 10% from that used for samples A and B.

X-ray diffraction (XRD) experiments were performed at beam line X-20C of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using a wavelength of 1.54 Å. Electron microscopy studies were carried out on cross-sectioned samples using a JEOL 4000EX high-resolution electron microscope operated at 400 keV.
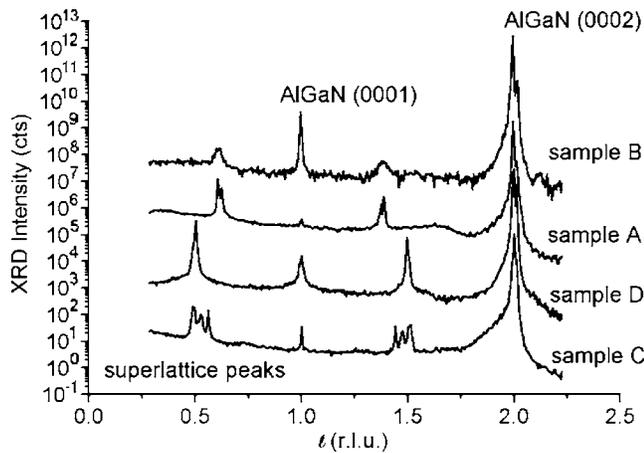
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FIG. 1. On-axis XRD spectra of four AlGaN samples vs reciprocal lattice unit. Several superlattice peaks are clearly observed (curves are translated vertically for clarity).

In the case of a completely random $Al_xGa_{1-x}N$ alloy, the average atomic scattering factors at each cation site are equal. Hence, for on-axis XRD ($h=k=0$), Bragg reflections with an odd index l are forbidden. Figure 1 shows the θ-2θ XRD patterns of the $Al_{0.72}Ga_{0.28}N$ films as a function of wave number in reciprocal lattice units (r.l.u.). In addition to the expected AlGaN (0002) peak, all four samples show superlattice peaks indicative of atomic ordering. These additional peaks indicate the presence of superlattice structures with different periodicities. The widths of the superlattice peaks suggest that the ordered regions vary from approximately 20 nm to more than 70 nm thick.

For sample D, there are superlattice peaks at $l_1=0.5$ and at the symmetric position $l_2=2-l_1=1.5$. These superlattice peaks suggest the presence of order with a periodicity of $2c$ (c being the wurtzite lattice constant in the z direction; 1 ML is $c/2$), i.e., 4 ML. Films grown in more Ga-rich environments exhibit superlattice peaks that are much more complex. Sample C has a triplet of peaks at $l_1=0.492$, $l_2=0.528$, and $l_3=0.562$ as well as the symmetric positions $2-l_{1,2,3}$. We note that reflections at the symmetric positions rule out the possibility that the phase(s) could correspond to material with a significantly different lattice parameter than that of the film itself (0.501 nm). A possible interpretation of the observed diffraction patterns is that the peaks are due to the presence of a modulated phase with a modulation wave number $(l_2-l_1)=(l_3-l_2)=0.036$ r.l.u., corresponding to a repeat distance of $27.8\pm0.9c$. The observed peak positions thus have no clear relationship with the crystal lattice, suggesting that they represent an incommensurate phase(s).

For sample A, double peaks are observed at $l_1=0.608$ and $l_2=0.624$, as well as the symmetric positions $2-l_{1,2}$. These are again incommensurate positions with respect to the crystal lattice. There are broad maxima at $l_3=0.368$ and $2-l_3$, which are also incommensurate positions. Sample B, grown under similar conditions to sample A but doped with Si, also exhibits peaks at $l_1=0.608$ and the symmetric position $2-l_1$, but they are lower and broader than for sample A.

In all cases, a clear $l=1$ [i.e., (0001)] peak is observed in addition to the incommensurate peaks. Since the Si(111) monochromator rejects even harmonics, this peak cannot be simply a harmonic reflection from the (0002). It must either be due to ordering or due to strains arising from dislocations or stacking faults. Here we will use the term "stacking fault"

to refer only to changes in cation layer structure sequence (e.g., between wurtzite and zincblende structures)—not to changes in cation occupation probabilities within a fundamentally wurtzitelike structure. The ideal wurtzite structure has the hexagonal close packing with alternating A and B layers whereas the cubic zinc blende structure has the *ABC* face-centered-cubic layer sequence. In the absence of induced strain, stacking faults between zinc blende and wurtzite structures do not cause significant peaks at odd integer positions in the (000l) direction. However, strain introduced by such stacking faults can give rise to such peaks. In fact, electron microscopy studies of these materials shows that the density of stacking faults is relatively low and that there appears to be no significant variation between samples in the density of threading dislocations. We must therefore attribute the variations in $l=1$ peak intensity as primarily due to differing degrees of cation ordering.

To provide further insight into the nature of the incommensurate ordering, the films were examined by electron microscopy. Selected area diffraction (SAD) patterns were recorded at $\langle1\bar{1}00\rangle$ and $\langle11\bar{2}0\rangle$ zone axes. The former are shown in Fig. 2; the strong spots represent Bragg reflections due to the wurtzite structure. The faint extra spots visible between the Bragg reflections confirm the presence of superlattice structures with long-range ordering; the positions of these spots correspond closely to the superlattice peak positions observed by XRD in Fig. 1. The streaking visible along the [000l] direction in the SAD patterns as well as the high background in the XRD scans indicate that there is significant disorder in the cation ordering sequence. The electron micrographs show that different kinds of order coexist in the same sample, separated by domain boundaries. Evidence of this can be seen in the diffuse peak at approximately $l=1.66$ from sample A in Fig. 1. It is noteworthy that the SAD patterns from the regions of complex order (Fig. 2) also show the (0001) peak, suggesting that it originates from the incommensurate phase. If the (0001) peak is indeed from the incommensurate phase, then its presence suggests that the complex ordering might be built from a modulated two-layer ordering.

The chemical ordering observed here in samples with growth conditions of group-III/N ratio greater than or equal to 1 is clearly more complicated than those previously reported.[2,6,10] Iliopoulos *et al.*[2] have suggested that a small tilt found in their films might be due to substrate miscut and that it could lead to complex ordering via the mechanism proposed by Venezuela *et al.*[18] However, we observe no systematic ordering behavior with substrate miscut in the samples reported here; indeed, we observe coexistence of different orderings within the same sample.

In considering possible ordering mechanisms, it is important to note the change in ordering observed between sample D, grown under nitrogen-rich conditions (and hence presumably little or no Ga-overlayer) and showing only 4 ML ordering, and the other samples grown with higher Ga/N ratios and showing more complex incommensurate structures. Moreover, sample C, showing perhaps the most complex ordering behavior, was grown in an environment with Ga surplus, presumably leading to a thicker overlayer during growth. Finally, samples A and B, grown with similar group-III/N ratios, exhibit similar incommensurate ordering. Sample B, with *n*-type Si doping, is less well ordered than A.
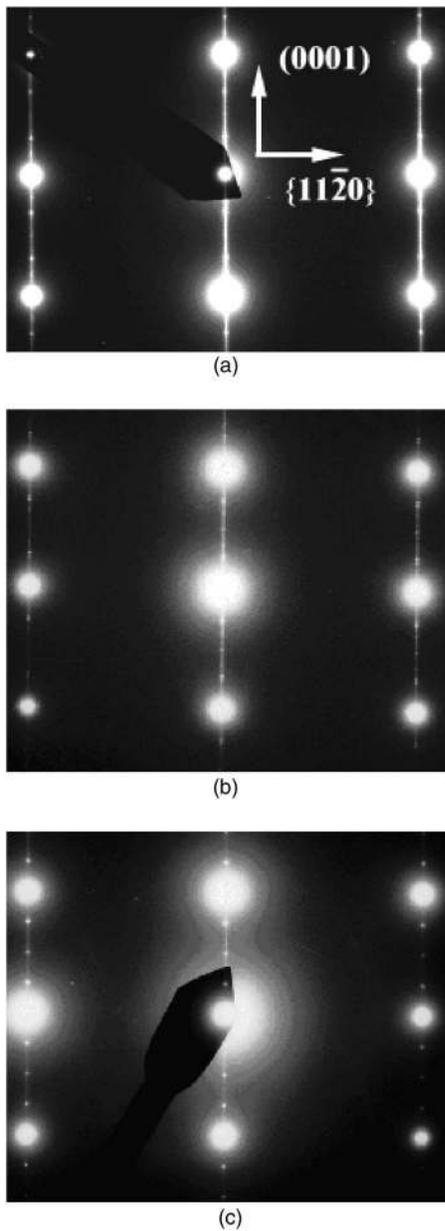
FIG. 2. TEM-SAD patterns of (a) sample A, (b) sample C, and (c) sample D.

It is believed that the presence of Si could interfere with the development of a Ga autosurfactant overlayer on the growing film, which suggests that the Ga-overlayer plays an important role. The Ga overlayer on the surface of the growing nitride film is thought to be highly mobile,[16] and presumably also increases the mobility of other species in the overlayer. The enhanced diffusion rates in this surfactant layer may provide more lateral homogeneity than would be possible for growth directly from the vapor, allowing the growth of well-defined ordered structures in a manner that would not otherwise be possible because of lateral inhomogeneity.

As a possible ordering mechanism in which the surfactant layer might play a crucial role, we consider that the rate of Ga and Al incorporation into the growing film is likely to be dependent on the difference in chemical potential between the film and the surfactant layer for each cation species. Moreover, the chemical potential of each element in the near-surface region of the film will also depend upon the lattice parameter of the film at the surface, which may change

slightly with surface composition. Hence, if the local film composition is high in Al at some time, there may be a tendency to continue incorporating Al from the surfactant layer at a faster than average rate. This would deplete Al in the overlayer, causing it to become more Ga rich and leading to a change to more Ga incorporation. Such a mechanism would not depend on the lattice geometry, and could easily be incommensurate.

In summary, $Al_{0.72}Ga_{0.28}N$ samples grown on *c*-plane sapphire by PA-MBE using different group-III/N growth ratios exhibit complex ordering dependent upon the growth conditions. Nitrogen-rich growth produced ordered structures of 4 ML, whereas more Ga-rich growth produced incommensurate structures. The widths of the XRD superlattice peaks indicate that the ordered regions are more than 20 nm thick while electron micrographs confirm that structures with different orderings coexist in the same material. The increasing complexity and domain size of the ordering with increasing Ga growth condition suggest that the ordering is likely related to the presence of the Ga overlayer and the kinetics of cation incorporation from the overlayer into the growing film.

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