

# Domain structure in chemically ordered $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys grown by molecular beam epitaxy

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Observation of long range atomic ordering in InGaN films grown by molecular beam epitaxy on A-plane sapphire is reported, based on x-ray diffraction and transmission electron microscopy studies. The InGaN films have a domain structure, with alternating domains of ordered and disordered phases, close to the film/substrate interface. Closer to the film surface, disordered domains are no longer observed. The degree of ordering was found to increase with growth rate (at the low growth rates used in these materials), which is consistent with ordering being a surface phenomenon. © 1999 American Institute of Physics. [S0021-8979(99)04902-6]

## I. INTRODUCTION

The InGaN ternary system has, in recent years, attracted special interest because of its potential for the formation of light emitting devices operating in red to ultraviolet (UV) regions of the energy spectrum. Several designs of double heterostructures (DH), single quantum well (SQW) and multi-quantum well (MQW) structures using InGaN active layers have been successfully grown and processed to make light emitting diodes (LEDs) and laser diodes (LDs).<sup>1-4</sup> In spite of all these developments, the growth and properties of InGaN alloys have yet to be completely optimized or understood.

The difficulties in InGaN growth are mainly due to a very high equilibrium vapor pressure (EVP) of nitrogen over InN and a large lattice mismatch of 11% between InN and GaN. At the standard growth temperatures of GaN (750 °C), the EVP of nitrogen over InN is more than ten orders of magnitude greater than that over GaN.<sup>5</sup> Thus, the growth temperature of InGaN alloys is generally low to prevent dissociation. However, at low temperatures, indium droplets may form, which according to Piner *et al.*,<sup>6</sup> act as sinks for InN and prevent incorporation of higher indium content in the film. In addition, the crystalline quality of the film is inferior at lower growth temperatures due to poor surface mobility of the adatoms, resulting in three-dimensional growth. Furthermore, the large lattice mismatch between InN and GaN (which have very different tetrahedral radii) results in highly strained InGaN alloy, which could cause deviations from the randomness of the alloy. Recently, phase separation has been theoretically predicted and experimentally observed in these compounds, with indium greater than 35%.<sup>7-12</sup>

There have been extensive studies on III-V compounds with the zinc-blende structure, to investigate their deviations from randomness. Zunger and Mahajan have reviewed several observations, which indicate that when the tetrahedral radii of the atoms in a particular sublattice are different,

structural variations are observed in the form of phase separation and/or atomic ordering.<sup>13</sup> Extensive transmission electron microscopy (TEM) investigations with selective area diffractions (SAD) and dark field imaging have been reported that reveal phase separation as well as long range atomic ordering in these compounds.<sup>13-17</sup> Both these phenomena are believed to be two-dimensional in nature, occurring on the growth surface and then being trapped in the bulk due to kinetic limitations. Atomic ordering in these compounds is believed to be caused by surface-reconstruction induced subsurface stresses which force preferential occupation of sites by atomic species of different radii.<sup>15</sup> Recently ordering has been reported in  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  alloys<sup>18</sup> and in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys<sup>11,19-21</sup> based on x-ray diffraction (XRD) and TEM studies.

In this report, we present our observations of the domain structure of ordered and disordered phases in InGaN films grown at 650–675 °C. We also report the influence of the growth parameters on ordering, to develop insights regarding the ordering mechanism.

## II. EXPERIMENTAL METHODS

Bulk  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films were grown on A-plane sapphire substrates by a three-step process similar to GaN growth.<sup>22</sup> Sapphire substrates were first nitridated by exposing their surface to an electron cyclotron resonance (ECR) nitrogen plasma at 800 °C. This step was followed by the deposition of a low temperature GaN buffer of 200–300 Å thickness at 550 °C. The InGaN films were grown in the temperature range of 650–675 °C, to a thickness of 0.5–1 μm. By varying the fluxes of group III elements, the growth rate of the investigated films was varied from 5 to 50 Å/min. The structure of the films were characterized by reflection high energy electron diffraction (RHEED), scanning electron microscopy (SEM), XRD, and TEM measurements. X-ray diffraction studies were done on a four-circle, double crystal diffractometer using  $\text{Cu-K}\alpha_1$  radiation, monochromated by the (111)

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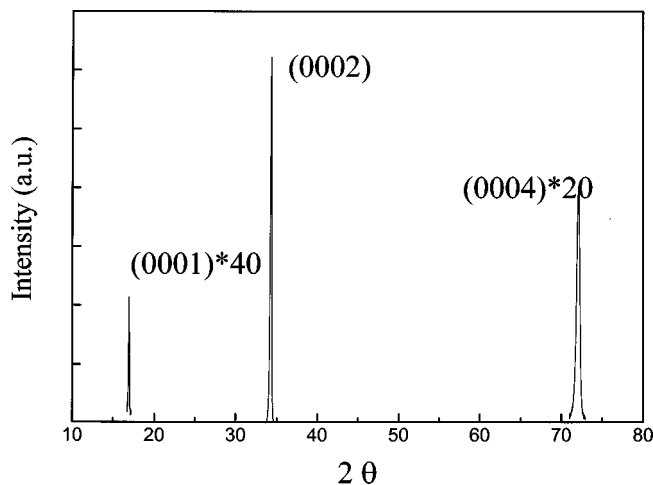


FIG. 1. X-ray  $\theta$ - $2\theta$  patterns from  $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$  film showing the presence of superlattice (0001) peak, indicating ordering.

plane of a Ge single crystal, which does not allow  $\lambda/2$  harmonic of the x-ray beam. The  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy composition was determined by calculating the lattice spacing from the (0002) Bragg reflection peak which was calibrated with reference to the (11-20) sapphire peak, assuming that Vegard's law is applicable for the  $\text{InN}$ - $\text{GaN}$  system. The  $d$  spacings for the (0002) Bragg reflections of pure  $\text{InN}$  and pure  $\text{GaN}$  were taken to be 5.7 and 5.18 Å, respectively. The calculated indium compositions were further confirmed by energy dispersion spectra (EDS) in a SEM. Cross-sectional TEM studies were carried out in a JEOL 2000FX, operated at 200 kV.

### III. RESULTS AND DISCUSSION

In an ordered alloy, the atoms occupy certain sites in the lattice preferentially, resulting in the appearance of forbidden reflections. The structure factor for  $(000\ell)$  planes, where  $\ell$  is odd, is zero in a random  $\text{InGaN}$  alloy with wurtzite structure. When the alloy is ordered, the indium atoms preferentially occupy lattice sites in alternating basal planes resulting in nonzero structure factors for  $(000\ell)$  planes. Figure 1 is a XRD scan from  $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$  film, which clearly shows the presence of (0001) peak, indicating atomic ordering in the alloy. Xiao *et al.* have observed a (0001) XRD peak in pure  $\text{GaN}$  due to defect ordering, but the (0001)/(0002) ratio in this case was only  $10^{-6}$ ,<sup>23</sup> which is about 4 orders of magnitude less than what we observe in  $\text{InGaN}$  films, implying that the ordering is not defect related. Furthermore, we have not observed such a superlattice peak in any of our  $\text{GaN}$  samples. We have observed similar atomic ordering in several  $\text{InGaN}$  films with indium concentrations ranging from 5% to 38%. The intensity of the superlattice peaks increased with indium composition, in general. However, in the films with indium greater than 20% in which chemical inhomogeneity was observed, the degree of ordering was significantly lower, which is attributed to a "competition" between the two strain relieving mechanisms: phase separation and ordering. Details of these studies have been published recently.<sup>11</sup> The 9% indium film being reported here exhibits no phase separation or chemical inhomogeneity.

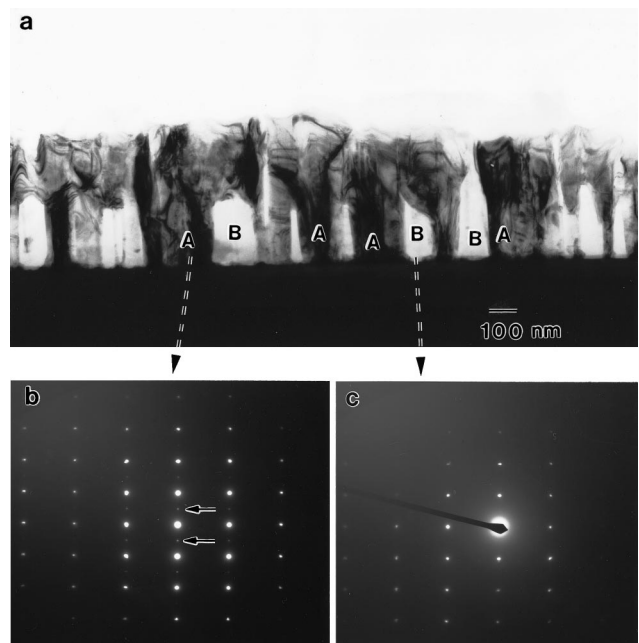


FIG. 2. (a) Cross-sectional TEM micrograph showing domain structure in  $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$  film, (b) SAD [10-10] pattern from the region marked "A," showing the presence of  $\{0001\}$  spots, (c) SAD [10-10] pattern from the region marked "B," where the  $\{0001\}$  spots are absent.

Ordering in these  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films was also observed in the TEM analysis, based on the appearance of (0001) superlattice spot. The microstructure of one of the  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films imaged with the (0001) spot is shown in the cross-sectional TEM micrograph in Fig. 2(a). The  $\text{In}_x\text{Ga}_{1-x}\text{N}$  film was 1  $\mu\text{m}$  thick and was grown with 9% indium. A domain structure is clearly seen near the interface, with a domain size of 100–200 nm. Two types of domains with different contrast are identified and designated as types A and B. SAD patterns obtained from the two regions is shown in Fig. 2. Figure 2(b) is a [10-10] diffraction pattern from region A, clearly showing the (0001) spot, which is an evidence of long range atomic ordering. The (0001) diffraction spots were also seen in the [11-20] selected area diffraction pattern, after tilting to illuminate the single row of  $(000\ell)$  spots, where there is no double diffraction contributing to the presence of (0001) spot. The pattern from region B does not have the superlattice (0001) spot [Fig. 2(c)], indicating a disordered structure. From the above observations, it is clear that  $\text{In}_x\text{Ga}_{1-x}\text{N}$  growth occurs with a domain structure with a mixture of ordered and disordered domains near the interface. The micrograph in Fig. 2(a) also shows that this domain structure is not present near the surface. Electron diffraction studies reveal that film is ordered near the surface across the entire film. We speculate that this is a result of heteroepitaxial stresses near the interface, which may promote the domain structure. We are currently investigating to further understand the mechanism of the domain formation.

The intensity of the (0001) superlattice peak is a good indicator of the degree of ordering in the film. We found that the degree of ordering depends on growth parameters such as growth temperature and growth rate, by comparing the intensities of the x-ray diffraction (0001) superlattice peaks from

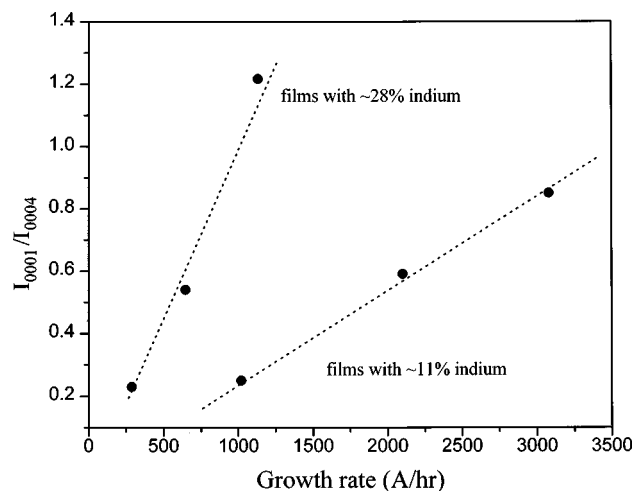


FIG. 3. Variation in (0001)/(0004) peak intensities with growth rate, in InGaN films grown under same conditions.

different samples. To account for the variations in x-ray intensity, film thickness, orientation etc., the relative intensities of (0001) and (0004) peaks are considered. Figure 3 shows the variation of the degree of ordering with growth rate for two sets of films, each set grown under identical conditions, except for the growth rate. The first set of data is for films with ~28% indium and the second set for 11% indium. It is clear that the degree of ordering increases monotonically with the growth rate in both sets of films studied.

Dependence of ordering on growth rate has been previously observed in other III–V alloys (arsenides and phosphides) with zinc blende structure. However, these alloys showed a decrease in the degree of ordering with growth rate, which is opposite to our observations. Theoretical total energy calculations in the zinc blende alloys showed that the ordered phase is stable at the surface, but is unstable within the bulk.<sup>24</sup> However, ordering induced at the surface during growth is retained during further growth due to kinetic limitations. We believe our observation of an increase in ordering with growth rate results from the relatively slow growth of the InGaN alloys in general. The relatively slow arrival rate of atoms at the surface provides sufficient time for surface ordering to occur. Once the ordered surface moves into the bulk due to continued deposition, the ordered phase is stabilized due to kinetic limitations. Thus for faster growth rates, the time spent in the near surface region is smaller, allowing for a smaller extent of disordering to occur. This strongly supports the contention that ordering is a surface phenomenon. We believe that the apparent contradiction with the observation in cubic III–V alloys is due to much faster growth rates (1–3  $\mu\text{m/h}$ ) used in these materials, which make surface ordering the kinetic rate limiting step, as opposed to subsurface disordering in our case (growth rate of 300–3000  $\text{\AA/h}$ ).

It should be stressed that the results reported in this article as well as in the previous reports of ordering in III–V nitrides<sup>11,18–21</sup> show that both the growth and the ordering occur along the (0001) plane, which has the same close packed symmetry as the (111) plane of the cubic alloys. However, ordering has not been observed<sup>25</sup> in such alloys

during growth on (111) planes. Currently, we do not have an explanation for this apparent contradiction. The theory of ordering in the wurtzite nitride alloy has not yet been developed. Recent RHEED studies<sup>26</sup> suggest that surface reconstructions in GaN depend strongly on the polarity of the surface. As discussed by Smith *et al.*,<sup>26</sup> our growth method of beginning with nitridation leads to a N-terminated face ([000-1] polarity). In agreement with these workers, we also found  $1\times 1$  reconstruction along the [11-20] azimuth of the RHEED pattern. First principle total energy calculations demonstrate that this  $1\times 1$  surface consists of a Ga monolayer (or adlayer) bonded to the uppermost N-terminated bilayer.<sup>27</sup> This adlayer is under tensile stress due to smaller preferred Ga–Ga bond length compared to the GaN lattice constant. The correlation of the observed ordering in III-nitride alloys with this surface structure and the stresses needs theoretical verification.

#### IV. CONCLUSIONS

We observed chemical ordering in InGaN alloys with a wide range of compositions. The films were found to have a domain structure, with alternating domains of ordered and disordered phases closer to the film/substrate interface. The disordered phase is not present closer to the surface of the film. The degree of ordering in the InGaN film was found to increase with the growth rate. The results are consistent with the notion that ordering is a surface phenomenon.

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