

PHASE SEPARATION AND ATOMIC ORDERING IN AlGaInN ALLOYS

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ABSTRACT

This paper reviews experimental results of phase separation and atomic long-range ordering in AlGaInN alloys, grown by plasma-assisted MBE. Phase separation has been observed in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys and atomic ordering has been observed in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys, using XRD studies. Specifically, we find that alloys with In content in excess of 30% show an extra diffraction peak corresponding to an alloy with high In concentration (close to pure InN). The effect of phase separation on the optical properties of the films was also investigated by transmission and photoluminescence measurements. From these studies, we find that the degree of phase separation depends on the thickness of the alloy layer. Atomic long-range ordering has been observed in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys over the entire alloy composition. The phenomenon was investigated by studying the superlattice peaks (0001), (0003) and (0005). The relative intensity of these peaks was found to be largest for the Al content in the 40-50 % range in qualitative agreement with expectations for an ordered structure of ideal $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ stoichiometry. We found that the ratio of III/V fluxes has a significant effect on the degree of ordering.

INTRODUCTION

The solid solutions of III-V compounds were originally considered to comprise of a random substitution of the mixed atoms. However, it was found over the past several years that there are deviations from perfect randomness due to either phase separation or atomic ordering during the growth of nominally homogeneous epitaxial layers [1]. In fact, the majority of III-V ternary and quaternary alloys are predicted to be thermodynamically unstable at the low growth temperature and show tendency towards clustering and phase separation [1,2]. Thus, atomic ordering was not expected to occur during the epitaxial growth of these materials. However, atomic long range ordering has been observed in a number of epitaxial III-V alloy semiconductors. Such include, for example, InGaAs grown on InP [3], AlGaAs grown on GaAs [4], and InGaP grown on GaAs [5] and many other III-V semiconductor alloys. Such phenomena were primarily observed in epitaxial films and the degree of ordering was found to depend strongly on growth conditions, such as growth method, substrate nature and orientation, surface step structure of the starting substrate plane, substrate temperature, III/V flux ratio, etc. The fact that the degree of ordering and the structure of the ordered alloys depend on the growth conditions strongly suggests that growth kinetics are the dominant factors, which lead to the long range ordering rather than intrinsic thermodynamic stability of the long range ordered phases [6].

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Evidence has recently been presented that these phenomena have a significant effect on the optical and electronic properties of the alloys [1].

Similarly, the solid solutions of III-V nitrides were considered until recently to be homogeneous random alloys. However, there is ample recent evidence of phase separation and atomic long range ordering in InGaN and AlGaN alloys [7-10]. The study of such phenomena in these alloys is important since these materials are currently employed in various optical and electronic devices. In this paper, we present our recent results in phase separation and atomic long range ordering in InGaN and AlGaN alloys.

EXPERIMENTAL METHODS

Both the InGaN and AlGaN alloys were grown by plasma-assisted molecular beam epitaxy (MBE). The deposition system consists of a Varian GEN II MBE unit equipped with an ASTeX compact electron cyclotron resonance (ECR) plasma source for activating the nitrogen. The group III elements and the dopants (Si, Mg) are evaporated from regular effusion cells. The design of the ECR source, for producing sufficient amount of activated nitrogen for the growth of high quality GaN films at a growth rate of 200-300 nm/h, was reported previously [11]. The films were grown on (0001) sapphire substrates, which were first subjected to plasma nitridation (conversion of the surface of Al_2O_3 to AlN) and then coated with 30nm low temperature GaN buffer [12]. The InGaN films were grown at 650 to 700°C at growth rates between 10-30 Å/min, which is of the same order as those of InGaN films grown by the metal-organic chemical vapor deposition (MOCVD) method [13]. The AlGaN films were grown at 750°C at growth rates of 25-35 Å/min. During the growth of these films, a number of deposition parameters such as the ratio of the III/V fluxes and the degree of n-type doping, were varied.

The structure of the films was determined by x-ray diffraction (XRD) using Cu $K\alpha_1$ and Co radiation in a four circle diffractometer with a Ge (111) single crystal monochromator that forbids x-ray reflection of the $\lambda/2$ harmonic. The composition of the films was determined from the XRD peaks assuming that Vegard's law is applicable in these ternary alloy systems. The InGaN films were also characterized by optical absorption and photoluminescence studies as reported earlier [7-9].

EXPERIMENTAL RESULTS AND DISCUSSION

A. Phase separation in InGaN Alloys

Phase separation in InGaN alloys was studied in thick (300-400 nm) InGaN films or thinner (<50 nm) InGaN films in the form of InGaN/GaN double heterostructures or InGaN/AlGaN MWQs. The phenomenon was studied directly using XRD or indirectly by determining the optical properties of the films through transmission and photoluminescence measurements. These InGaN films or structures were grown on top of thick GaN films on (0001) sapphire substrates.

All InGaN films were examined by scanning electron microscopy (SEM) and found to have mirror-like surfaces and show no evidence of indium droplets. The full width of half maximum (FWHM) of the θ -2 θ XRD peaks for InGaN (7-9 arcmin) is greater than the FWHM of the corresponding GaN Bragg peaks (3-4 arcmin). The broadening of the InGaN peaks is

probably the combined effect of alloying, inhomogeneous strain and finite domain size effects [14]. X-ray diffraction of the thick $\text{In}_x\text{Ga}_{1-x}\text{N}$ films with InN mole fraction greater than 30% show an additional peak which corresponds to In concentration very close to that of pure InN [7-9]. Figure 1 shows the θ -2 θ XRD pattern for an InGaN film with 37% InN mole fraction. This result represents the first observed evidence of phase separation in InGaN films. Recently, a similar result was reported for films grown by the MOCVD method [15].

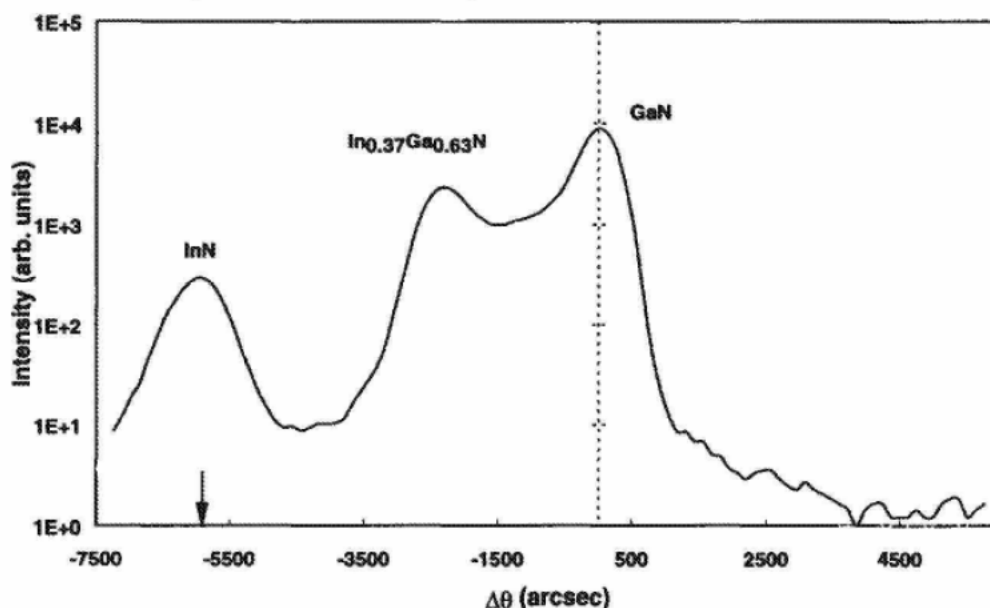


Fig. 1: Logarithmic plot of the XRD data for an $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$ sample

XRD studies of InGaN/GaN double heterostructures with the thickness of the InGaN less than 50nm show no evidence of phase separation as described previously. Figure 2 shows the XRD patterns for two such double heterostructures with InN mole fraction 53% and 81% respectively. This result can be accounted for by taking into account that phase separation in any alloy requires long range diffusion and thus a correlation should exist between phase separation and length of time required for the growth of the film. We believe that this is one of the reasons for the non-observable phase separation in GaN/InGaN/GaN double heterostructures with thin InGaN layers. Strain associated with thin InGaN quantum wells could also stabilize the alloy against phase separation.

In addition to direct observation of phase separation by XRD, we also studied these phenomena indirectly by examining the effect of phase separation on the optical properties of the films. Figure 3 shows the optical absorption constant versus wavelength for three films with InN mole fraction of 0, 18 and 37% respectively. It is obvious from these data that while the low In concentration films have a single absorption edge, the film with 37% In has two distinct absorption edges, characteristic of a composite structure. However, from the data of Fig. 3, it is

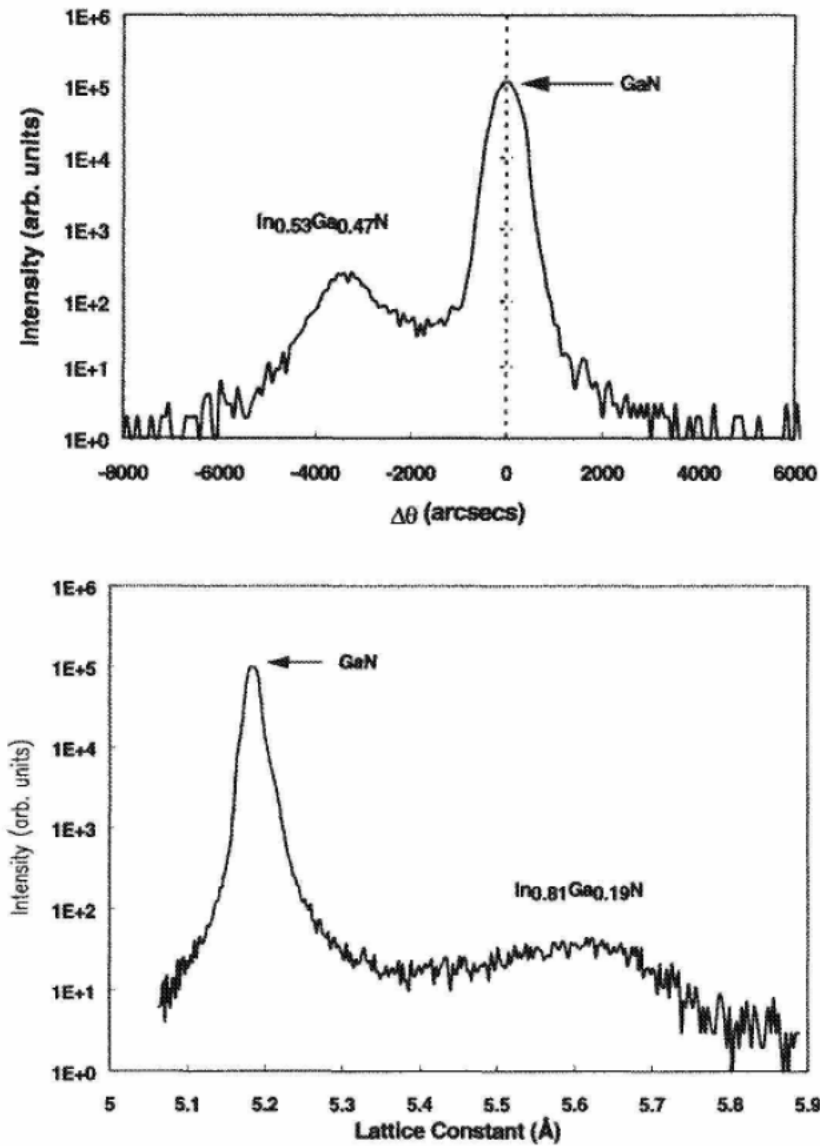


Fig. 2: XRD data for (a) GaN/In_{0.53}Ga_{0.47}N and (b) GaN/In_{0.81}Ga_{0.19}N double heterostructure

difficult to determine the optical gap since the optical absorption constant of any direct gap semiconductor consists of the region in which the energy of the photon is greater than the bandgap (Kane region) and that in which the energy of the photon is less than the bandgap (Urbach edge). The optical absorption constant in the two regions is given by the following expressions respectively[16]:

$$\alpha \propto \sqrt{E - E_g} \quad (1)$$

$$\alpha = \alpha_0 \exp\left(\frac{E - E_1}{E_0}\right) \quad (2)$$

where α_0 and E_1 are independent of either thermal or structural disorder.

An accurate determination of the optical bandgap can be accomplished by using the derivative of the optical absorption constant [16]. The derivatives of equations (1) and (2) are:

$$\frac{d\alpha}{dE} \propto \frac{1}{\sqrt{E - E_g}} \quad (3)$$

$$\frac{d\alpha}{dE} \propto \exp\left(\frac{E - E_1}{E_0}\right) \quad (4)$$

From equations (3) and (4), the derivative of the absorption constant at the Kane regime depends as $1/\sqrt{E - E_g}$ while the derivative of the absorption constant at the Urbach edge has the same exponential dependence on E . A plot of the derivative of the absorption constant versus the energy, for the samples described in Fig. 3, is shown in Fig. 4. According to these data the bandgap of pure GaN is 3.37 eV. The bandgap of the InGaN film with 18 % Indium is 2.74 eV with a broad Urbach edge. The film with 37 % indium appears to have two gaps at energies 2.75 eV and 1.9 eV

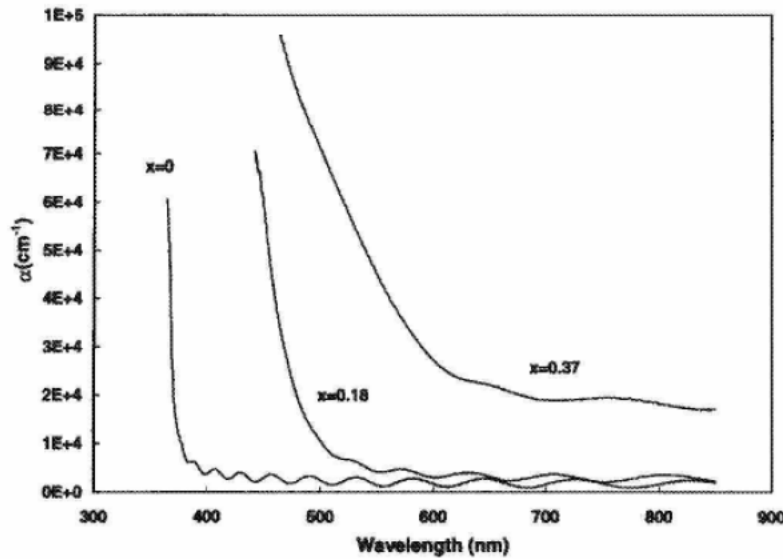


Fig. 3: Optical absorption data for $\text{In}_x\text{Ga}_{1-x}\text{N}$ samples with $x=0$, $x=0.18$ and $x=0.37$ and 1.9 eV.

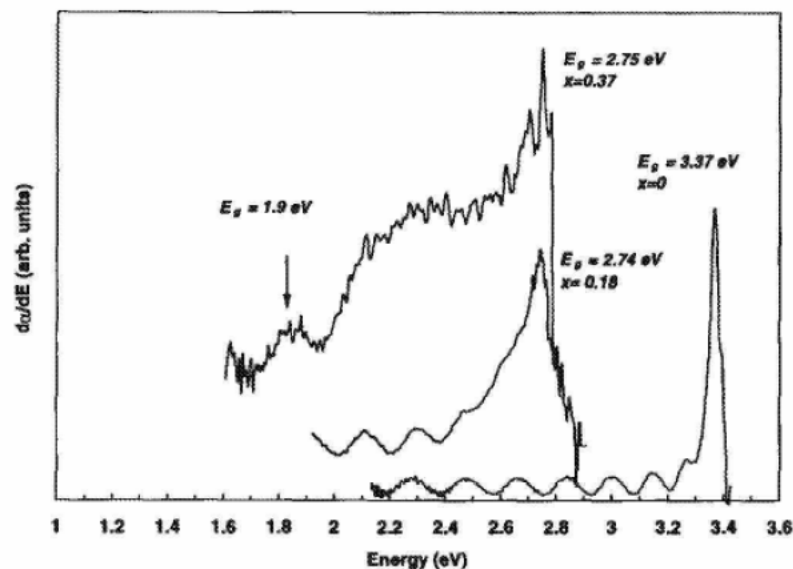


Fig. 4: dR/dE vs photon energy for the samples discussed in Fig. 3

Evidence of phase separation in InGa_N films, based on optical absorption data has also been reported in films grown by the MOCVD method [17]. In Fig. 5, we reproduced the optical

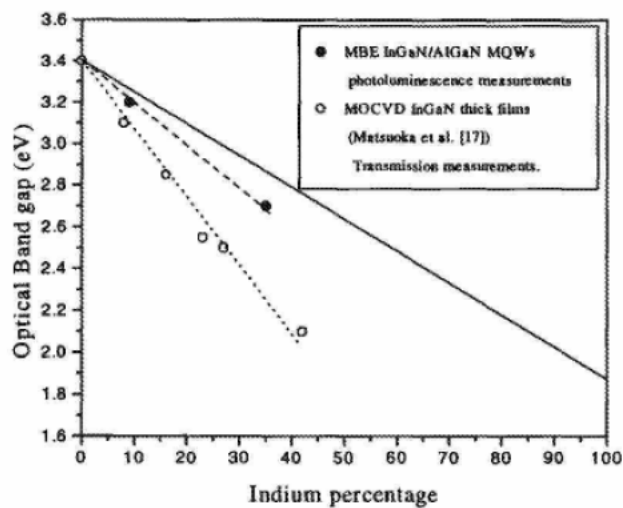


Fig. 5: Optical bandgap vs InN mole fraction for the InGa_N films and InGa_N/AlGa_N MQWs described in the inset of the figure.

bandgap data from reference [17]. The solid line represents the relationship between optical bandgap vs. InN mole fraction, assuming the validity of Vegard's law. It is important to note that the data points for the bulk films fall significantly below the straight line, a result which can be accounted for by phase separation in such films. For example, the film with 42 % indium has approximately the same optical gap as that of pure InN, which is consistent with the data of Fig. 1. Plotted in Fig. 5 are also the optical gaps, determined from the peaks of the photoluminescence, for two MQWs of InGaN/AlGaIn in which the InGaIn wells are about 100 Å thick [18]. The fact that these points fall closer to the straight line, supports our earlier conclusion that phase separation increases with the film thickness or duration of film growth.

Phase separation in the InN-GaN pseudo-binary system is thermodynamically expected because of the large difference in lattice parameter between GaN and InN (11 %). In a previous paper [9], we have estimated the maximum value of the critical temperature for miscibility in this system using the delta lattice parameter model (DLP), developed by Stringfellow [19],

$$T_c = \frac{8.75K (\Delta a)^2}{4R (\bar{a})^{4.5}} \quad (5)$$

where Δa is the difference in the lattice constants of GaN and InN, $\bar{a}$ is the average lattice of GaN and InN and R is the gas constant. K is the proportionality constant between atomization enthalpy (bonding energy) and lattice constant in the Phillips and VanVechten formula [20] :

$$\Delta H^a = K a^{-2.5} \quad (6)$$

The constant K was found by Stringfellow [19] by fitting Eq. (6) to experimental data for III-V compounds to have a value of 1.17×10^7 cal/mol Å^{2.5}.

Equation (5) was derived for zincblende structure [19], while GaN and InN, in their equilibrium phases, have the wurzite structure. However, the cohesive energies of these two allotropic forms must differ only slightly [21]. Using the lattice constants for zincblende GaN and InN, we found from Eq. (5) that $T_c = 2457$ K. Based on this estimate, the growth of InGaIn alloys at about 1000 K occurs within the miscibility gap of this system. Recently Ho and Stringfellow [22] have used the valence-force-field (VFF) model with a number of nearest neighbors allowed to relax, and calculated a much lower $T_c = 1500$ K. However, even such a value is much higher than the typical growth temperature of InGaIn alloys. Thus, thermodynamically phase separation is expected in InGaIn alloys. However, it is very likely that growth kinetics also play a very important role in these phase separation phenomena.

B. Long Range Order in AlGaIn Alloys

Since AlGaIn alloys crystallize in the wurzite structure, the geometrical structure factor for the Bragg reflection (hkl) is given by the expression,

$$F_{hkl} = f_A + f_B e^{\{2\pi i(\frac{h+2k}{3} + \frac{l}{2})\}} \quad (7)$$

where f_A and f_B are the average atomic scattering factors of the (Al, Ga) atoms occupying the (000) and (1/3, 2/3, 1/2) sublattice sites of the hexagonal cell respectively. When the two sites are

occupied by the same atomic species or by random mixtures of the two species Bragg reflections with $l = \text{odd}$ and $(h + 2k) = 3n$ are forbidden according to Eq. (7). Thus, in pure GaN, pure AlN and random $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys, the (0001), (0003) and (0005) etc. diffraction peaks do not occur. However, if one of the sublattice sites is preferentially occupied by Al or Ga in an $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy, the two terms no longer cancel and superlattice peaks result.

Our group has recently reported that in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys, grown by MBE, the superlattice peaks (0001), (0003) and (0005) do exist [10]. Fig. 6 shows the θ - 2θ XRD pattern for an $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ alloy, in which the existence of superlattice peaks, in addition to the allowed diffractions, provides clear evidence of ordering in this sample.

In general, the superlattice structure factor of an ordered alloy can be written in terms of the long range order parameter $S = p_{\text{Al}}^1 - p_{\text{Al}}^2$, where p_{Al}^1 and p_{Al}^2 are the probabilities of finding aluminum on sublattice (000) or sublattice $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ sites respectively:

$$F_{hkl} = S(f_{\text{Al}} - f_{\text{Ga}}). \quad (8)$$

The long range order parameter must vanish at the compositional endpoints of pure GaN and pure AlN, so the superlattice peak scattering is expected to be largest in alloys with compositions

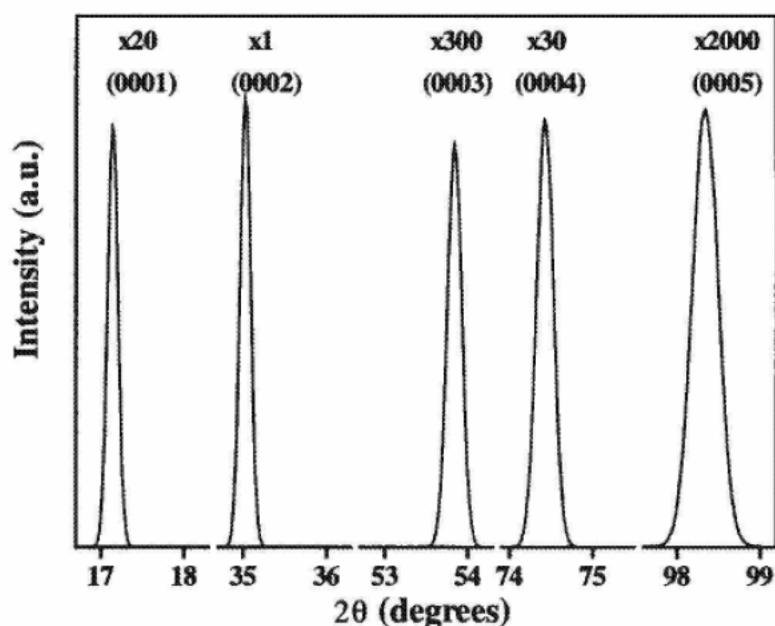


Fig.6: θ - 2θ XRD scan from an $\text{Al}_{0.5}\text{Ga}_{0.5}\text{N}$ sample, showing both the fundamental and superlattice peaks due to ordering

near 50%. Indeed, if the ordering was perfect, S would be proportional to x , where x is the composition factor of the minority component, and therefore in the kinematical scattering limit

[23] the superlattice peak intensity would increase with composition as x^2 . Figure 7 shows that the relative superlattice peak intensity is largest for films with relatively high concentrations of each component. Here the superlattice (0001) intensity has been normalized with respect to the (0004) fundamental intensity to account for differences in film thickness and orientational quality. The solid line in this figure was calculated from the expression:

$$\frac{I_{(0001)}}{I_{(0004)}} = \left[\frac{1 + \cos^2 2\vartheta_1 \cos^2 2\alpha}{\sin 2\vartheta_1} \right] \cdot \frac{(2x(f^{(1)}_{\text{GaN}} - f^{(1)}_{\text{AlN}}))^2}{(2(1-x)f^{(4)}_{\text{GaN}} + 2xf^{(4)}_{\text{AlN}})^2} \cdot \left\{ \frac{\sin \vartheta_4}{\sin \vartheta_1} \right\} \quad (9)$$

which represents the kinematical limit for perfectly ordered alloys, taking into account the Lorentz-polarization factor (in square brackets) and differences in film volume arising from illuminating the sample at different angles (in curly brackets) but neglecting the effect of absorption and the Debye-Waller temperature factor. In this expression, ϑ_k is the Bragg angle at the (000k) peak, $f^{(k)}_A$ is the scattering factor of molecule A at the (000k) peak and α is the Bragg angle of the monochromator. The experimental data are in qualitative agreement with the

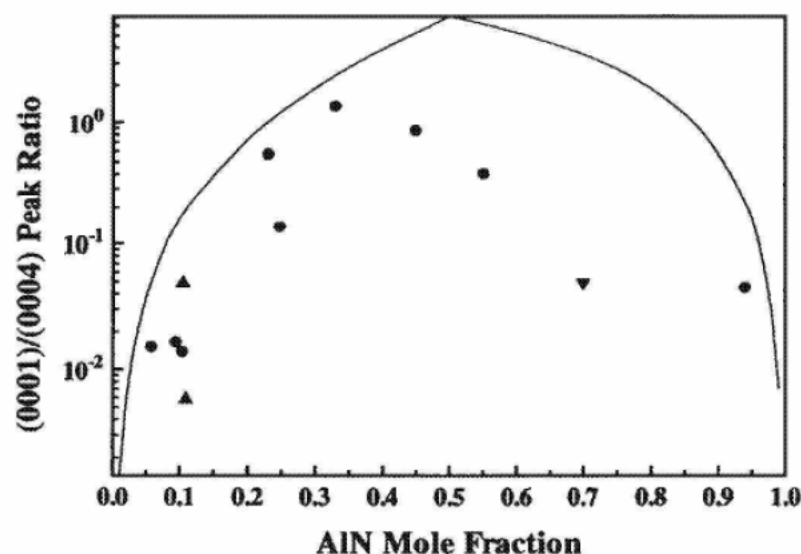


Fig. 7: Relative superlattice peak integrated intensity for a number of samples grown as a function of AlN mole fraction. Samples grown on sapphire are shown as circles and grown on 6H-SiC are shown as triangles. The solid line is the theoretical prediction in the kinematical limit.

theoretical prediction. However, the determination of the long range order parameter, S , from the experimental data of this figure, is not accurate because of dynamical scattering effects, surface roughness etc.

In addition we have also investigated the domain size, D , and the inhomogeneous strain, ϵ_{in} , of the grown films by examining the FWHM wavenumber, δk , of the fundamental and superlattice XRD peaks. The relationship between these quantities is given in reciprocal space by [24]:

$$\delta k = \frac{2\pi}{D} + \epsilon_{in} k \quad (10)$$

Figure 8 shows a plot of δk vs. k for an $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}$ film. To within the accuracy of our measurements the fundamental peaks indicate that the grain size of the alloy is 6400 Å which is comparable to the thickness of the film. From the same plot we observe that the superlattice peaks fall on a different line. This broadening of the superlattice peaks, compared to the fundamental peaks, can be attributed to either size effect broadening or formation of antiphase domains. In either case, we deduce that the average size of the ordered domains is somewhat less than the film thickness -- approximately 1700 Å. Since we do not have independent determinations of the Al composition we cannot determine homogeneous strain in those films utilizing the shift of the peaks. Therefore we cannot explore any dependence of lattice constant on the degree of atomic order.

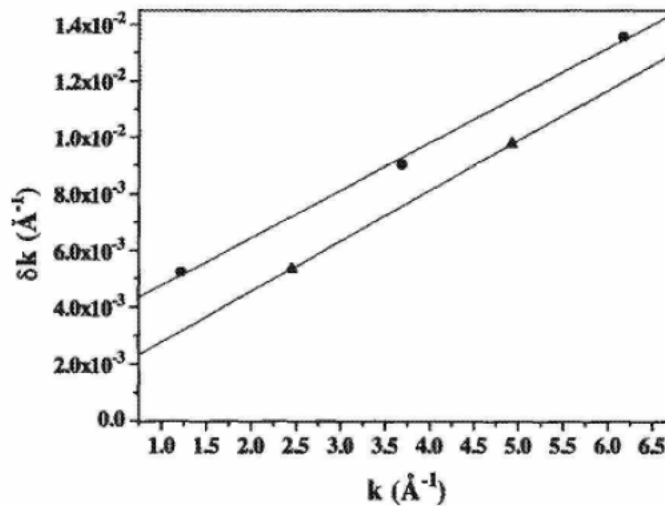


Fig. 8: Plot of δk vs. k for an $\text{Al}_{0.55}\text{Ga}_{0.45}\text{N}$ film grown on c -plane sapphire. The triangles indicate the fundamental peaks and the circles the superlattice peaks.

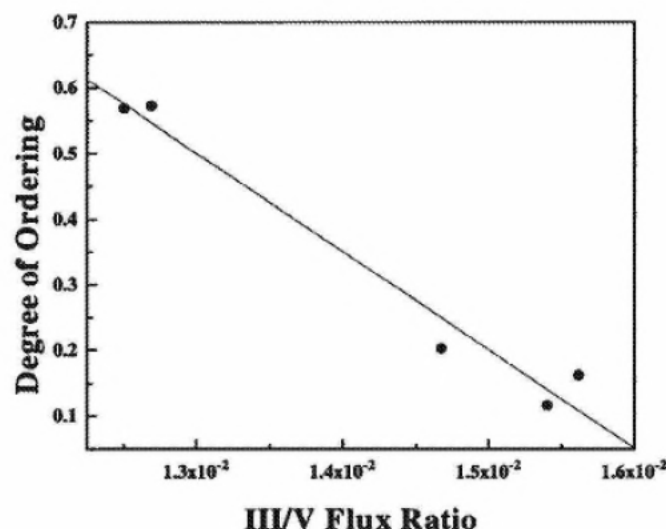


Fig. 9: Dependence of the degree of ordering on the III/V flux ratio for $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films grown under otherwise identical conditions

The long range ordering is expected to depend on a number of thermodynamic, growth and kinetic factors. In agreement with the findings reported in traditional III-V compounds, we found that the degree of ordering is affected by the ratio of III/V fluxes (see Fig. 9). More specifically, films grown at lower III/V flux ratios were found to have higher long range order. Furthermore, we observed that Si doping has a small effect in increasing the degree of ordering. Another parameter which most likely affects the long range ordering is the step structure of the substrate. However, we did not investigate this parameter systematically.

CONCLUSIONS

Experimental results on phase separation in InGa_N and atomic long range ordering in AlGa_N alloys produced by MBE were presented. Phase separation was directly observed by XRD in thick films with In_N mole fraction greater than 30%. However, such phenomenon was not observed in InGa_N/Ga_N double heterostructures or InGa_N/AlGa_N MWQs (InGa_N thickness < 50nm) with In_N mole fraction up to 80%. Phase separation was found to affect the optical properties of the films. We propose that the optical gaps in these composite films should be determined by plotting the derivative of the absorption constant versus energy. Phase separation in InGa_N alloys is thermodynamically expected. Using Stringfellow's DLP method, we calculated the maximum value of the critical temperature for miscibility in this system is 2457K, which is well above the growth temperature of these materials. Of course, kinetic factors could also play an important role in the phase separation of these materials.

Long range atomic ordering in AlGa_N alloys has been observed by studying the (0001), (0003) and (0005) superlattice peaks by XRD. We find that the ordering is largest for Al_N mole

fraction close to 50% in qualitative agreement with the kinematical scattering theory. The ordered domains in these films were found to be approximately one third of the thickness of the films. From the various kinetic factors, we found that the III/V ratio has a significant effect on the degree of ordering in these films.

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REFERENCES

- [1] A. Zunger and S. Mahajan, Handbook of Semiconductors, Vol. 3, 2nd Edition, edited by T.S. Moss (Elsevier, Amsterdam, 1994)
- [2] A.G. Norman, T.Y. Seong, L.T. Ferguson, G.R. Booker and B.A. Joyce, *Semicond. Sci. Tech.* **8**, 9 (1993)
- [3] H. Nakayama and H. Fujitsu, *Inst. Phys. Conf. Ser.* **79**, 289 (1986)
- [4] T.S. Kuan, T.F. Kuech, W.I. Wang and E.L. Wilkie, *Phys. Rev. Lett.* **54**, 201 (1985)
- [5] A. Gomgo, K. Kobayashi, S. Kawata, I. Hino, T. Suski and Y. Yudasu, *J. Cryst. Growth* **77**, 367 (1986)
- [6] H. Nakayama, M. Tochigi, H. Maeda and T. Mishino, *Appl. Surf. Science*, **82/83**, 214 (1994)
- [7] R. Singh and T.D. Moustakas, *Mat. Res. Soc. Symp. Proc.* **395**, 163 (1996)
- [8] R. Singh and T.D. Moustakas, *Electrochem. Soc. Proc.* **96-11**, 186 (1996)
- [9] R. Singh, D. Doppalapudi, T.D. Moustakas and L.T. Romano, *Appl. Phys. Lett.* **70**, 1089 (1997)
- [10] D. Korakakis, K.F. Ludwig Jr. and T.D. Moustakas, *Appl. Phys. Lett.* **71**, 72 (1997)
- [11] R.J. Molnar, R. Singh and T.D. Moustakas, *J. Electron. Mater.* **24**, 275 (1995)
- [12] T.D. Moustakas, R.J. Molnar, T. Lei, G. Menon and C.R. Eddy Jr., *Mat. Res. Soc. Symp. Proc. Vol.* **242**, 427 (1992)
- [13] S. Nakamura, *Microelectron. J.* **25**, 651 (1994)
- [14] R.W. Vook, Epitaxial Growth, edited by J.W. Matthews (Academic, New York, 1975), p.339.
- [15] A. Wakahara, T. Tokuda, Z. Dang, S. Noda and A. Sasaki, *Appl. Phys. Lett.* **71**, 906 (1997)
- [16] V. Ariel, V. Garber, D. Rosenfeld and G. Bahir, *Appl. Phys. Lett.* **66**, 2101 (1995)
- [17] T. Matsuoka, T. Sasaki and A. Katsui, *Optoelectron. Dev. and Tech.* **5**, 53 (1990)
- [18] R. Singh, D. Doppalapudi and T.D. Moustakas, *Appl. Phys. Lett.* **69**, 2388 (1996)
- [19] G.B. Stringfellow, *J. Cryst. Growth*, **58**, 194 (1982)
- [20] J.C. Phillips and J.A. Van Vechten, *Phys. Rev. B* **2**, 2147 (1970)
- [21] T.D. Moustakas, T. Lei and R.J. Molnar, *Physica B*, **185**, 36 (1993)
- [22] I. Ho and G.B. Stringfellow, *Appl. Phys. Lett.* **69**, 2701 (1996)
- [23] A. Guinier, X-Ray Diffraction, (Freeman, San Francisco, CA, 1963)
- [24] T. Lei, K.F. Ludwig Jr. and T.D. Moustakas, *J. Appl. Phys.* **74**, 4430 (1993)