Compositional Modulation in $In_xGa_{1-x}N$

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Abstract

Transmission Electron Microscopy and x-ray diffraction were used to study compositional modulation in In_xGa_{1-x} N layers grown with compositions close to the miscibility gap. The samples ($0.34 < x < 0.8$) were deposited by molecular beam epitaxy using either a 200-nm-thick AlN or GaN buffer layer grown on a sapphire substrate. In the TEM imaging mode this modulation is seen as black/white fringes which can be considered as self-assembled thin quantum wells. Periodic compositional modulation leads to extra electron diffraction spots and satellite reflections in x-ray diffraction in the $\theta-2\theta$ coupled geometry. The modulation period was determined using both methods. Larger modulation periods were observed for layers with higher In content and for those having larger mismatch with the underlying AlN buffer layer. Compositional modulation was not observed for a sample with $x = 0.34$ grown on a GaN buffer layer. Modulated films tend to have large " Stokes shifts" between their absorption edge and photoluminescence peak.

Key words: compositional modulation, InGaN, TEM, x-ray

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Introduction

$In_xGa_{1-x}N$ semiconductor materials are technologically important constituents in microelectronic and optoelectronic devices. They are used as the active layer in short-wavelength light-emitting diodes and lasers [1,2]. Use of these alloys together with GaN and AlN makes it possible to produce nitride-based light-emitting diodes operating from the ultraviolet well into the red. However, the large size difference between Ga and In atoms makes growth of $In_xGa_{1-x}N$ challenging, particularly for $x > 0.2$. A miscibility gap for this material was predicted theoretically and phase separation has been observed experimentally in films grown by Metalorganic Chemical Vapor Deposition (MOCVD) and Molecular Beam Epitaxy (MBE) for $x > 0.25$ [3-9].

Compositional fluctuations have been observed in several ternary and quaternary alloys such as InGaP [10, 11]. It was concluded that this compositional modulation was associated with spinodal decomposition driven by asymmetry in the elastic coefficients. Therefore, modulated waves can be formed to minimize the strain contribution to free energy in the solid solution. Chu et al [12] also reported modulated structures in the same alloys and showed that compositional modulation is developed on the surface during epitaxy and grows in the form of a columnar structure along the [100] and [010] directions.

There is a comprehensive review on phase separation and ordering written by Mahajan and Zunger [4]. These authors discussed lateral and vertical phase separation from both a theoretical and experimental point of view. Reports on vertical compositional modulation are less common; however vertical columns with compositional modulation along [100] direction were observed in the $Zn_{1-x}Mg_xS_ySe_{1-y}$ lattice matched to ZnSe buffer/GaAs substrate [13]. Chu et al [12] reported that one-dimensional compositional modulation starts at the growth surface and

gives rise to a tweed structure with domains of different tetragonality and with different composition.

Experimental

In$_x$Ga$_{1-x}$N films (0.3 < x < 0.8) in this study were grown by MBE. The samples were grown at the temperature range of 600 - 530°C (lower temperatures were used for a higher In content). The sample with the lowest In content (x = 0.34) was deposited on a GaN buffer layer grown on c-plane sapphire and remaining samples were deposited on a 200-nm-thick AlN buffer layer grown on sapphire. All of these compositions lie well within the miscibility gap predicted by Ho and Stringfellow and a strong thermodynamic driving force for spinodal decomposition is expected [3]. Transmission Electron Microscopy (TEM) together with energy dispersive x-ray spectroscopy (EDXS), "Z-contrast technique" and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope [14] and x-ray diffraction (XRD) have been used for structural characterization. JEOL 3010, Philips 300-kV modified CM30, and Philips Tecnai (200 kV) electron microscopes have been used for these studies. The same samples were also studied using photoluminescence (PL) and absorption studies.

Results

Classical electron microscopy and high resolution studies were used to study In$_x$Ga$_{1-x}$N layers with different composition. Using **g.b** analysis, it was found that edge dislocations dominated in the sample with x = 0.34 and their density was about 2×10^{10} cm^{-2}. Some increase in dislocation density (10^{11} cm^{-2}) was observed for a sample with higher In content (x = 0.5 or 0.55) grown on an AlN buffer layer. However for much higher In concentration x = 0.78 (grown on AlN), a decrease of the dislocation density to 6×10^{10} cm^{-2} was observed. The InGaN/AlN

interface was rough, with roughness up to 150Å measured along c-axis. In all three samples with In concentration x = 0.5, 0.55 and 0.78 white/black "tweed" - like fringes were observed (Figs. 1a). This tweed-like fringes were not observed in the sample with x=0.34 grown on GaN buffer layer. Low-magnification TEM micrographs indicate that black and white fringes are distributed mainly on planes inclined at angle ± 60° to the c-axis; however, in some areas, fringes perpendicular to the c-axis were also observed [15]. Modulated films tend to have large "Stokes shifts" between their absorption edge and photoluminescence peak; however, this does not appear to be systematically correlated with the modulation period (Fig. 1b)

The InGaN layers experience some columnar growth with columns separated by dislocations. It is observed that these black/white fringes are parallel within the column. However, in any place where dislocations (or inversion domains) intersect such columns, the fringe arrangements change slightly (by few degrees). The black/white fringes were observed in both [1$\underline{1}$00] and [11$\underline{2}$0] projections. Selected area diffraction patterns were taken from these layers with an aperture which included the AlN buffer layer and the Al_2O_3 substrate to obtain an internal standard for the measurement of interplanar distances in the InGaN layers (Fig. 2a). It was noticed that each diffraction spot from the InGaN layer was surrounded by extra diffraction "spots" suggesting a structure with possible periodic compositional modulation. These extra "spots" were in the form of small arcs, with maximum spread ± 40° around c-axis. The intensity distribution was not uniform within these arcs and clear maxima at about ± 32° relative to the c-axis in agreement with "w" pattern of the white/black fringes (Fig. 2b). Based on the measured distances from the main InGaN reflections and the center of the arc (equivalent to the extra spot along c-axis) the period of this modulation along c-axis was determined to be $\Delta = 45$Å for the

sample with x = 0.5, Δ = 47Å for the sample with x = 0.55, and Δ = 66Å for the sample with x = 0.78.

X-ray diffraction (XRD) in the θ–2θ coupled geometry using Cu-K$_\alpha$ x-rays revealed satellite reflections around the 0002 and 0004 InGaN peaks, confirming compositional modulation in these samples (Fig. 3). Determined value of the period was Δ = 47Å in the sample with x = 0.5 and Δ = 58Å in the sample with x = 0.78, which in reasonable agreement with those determined by TEM (45Å and 66Å, respectively). Differences may come from the fact that the areas studied by x-ray are much larger than those studied by TEM.

EDXS measurements across white/black fringes show systematically that the In-K$_\alpha$ peak decreases its intensity when Ga-K$_\alpha$ peak increases, confirming compositional modulation within the film [15]. The average estimated concentration on the black fringe was about 40% In and about 60% Ga. Based on these results, we can postulate that alternative layers of GaN (+In)/InN (+Ga) were formed.

Low-loss spectra together with Z-contrast imaging have been used to learn about chemical composition of black/white fringes in our samples. Using an annular dark-field detector, these dark/white fringes were observed in the entire sample, confirming that the fringe contrast is related to the compositional change. The brightest images are consistent with the element of the highest Z [14]. Therefore, bright fringes in our images were assigned to In and dark fringes to Ga (Fig. 4a).

Low-energy spectra (plasmon) show differences depending on whether the electron beam was placed on a white or black fringe. On the white fringe, the maximum of the low loss peak is observed at the energy of 24 eV (Fig. 4b). The position of this peak remains at the same energy

when the electron beam is placed on the black fringe but an additional peak also appear at the energy of 19 eV (Fig. 4c) superimposed on the peak with the maximum at 24 eV. Comparing our spectra with the EELS Atlas [16] this energy position is consistent with Ga. The difference also appears when $L_{2,3}$ edge of Ga is studied. The Ga edge has doubled intensity when the beam is placed on the black fringe [15], confirming our expectation based on Z-contrast imaging and EDX spectra. Unfortunately, In-K edge is only slightly shifted from the N-K edge and these edges cannot be observed separately. There were no difference in intensity of these two superimposed peaks on either fringe.

Discussion

Based on our characterization methods we see consistently that compositional modulation is taking place in $In_xGa_{1-x}N$ samples grown on AlN buffer layers for the compositions within $0.5< x < 0.78$. The reason for this modulation is still under investigation, but it appears that the mismatch strain between AlN and InGaN might play an important role (14% mismatch between InN and AlN). Single-phase material has been grown for x = 0.34 using a GaN buffer layer (2% mismatch between InN and GaN); this is a composition for which spinodal decomposition might be expected [3,4].

This compositional modulation in our samples is not strictly on c-planes. It appears that the fringes are mostly inclined to c-axis at about ± 60° making about ± 32° angle with this axis in the diffraction pattern. Columns separated by grain boundary dislocations with tweed–like pattern are formed and fringes within one column are mostly parallel to each other and form "W" pattern , however locally one can find fringes formed on c-plane. Since these tweed-like fringes can be observed in two perpendicular orientations: [1$\underline{1}$00] and [11$\underline{2}$0] arranged approximately at

same angle to c-axis we are expecting that the plane on which segregation is taking place must have six-fold symmetry and it can be close to {10$\underline{1}$3} plane.

Many ternary and quaternary alloys show either CuPt-type ordering on particular crystallographic planes like in GaInP alloys [17] or compositional ordering [5-13, 18]. In most cases, the compositional modulation was related to spinodal decomposition driven by asymmetries in the elastic coefficients and phases with different compositions have been formed [5-9]. There were also reports on compositional modulation developed on the surface during epitaxial growth, which resulted in a growth of columnar structures with nodules oriented along <100> or <010> directions [12]. Only in one case for the short period superlattices of GaAs/GaSb has axial compositional modulation been reported [18].

However, in our samples this compositional modulation appears somehow different than this discussed in the literature [3-13]. We noticed that the interface between AlN buffer layer and InGaN layers is not flat and growth of these ternary layers start on corrugated surfaces. Growth of the layers with a similar In content on GaN buffer layer start on much more planar surfaces and with much smaller lattice mismatch and compositional modulation is not observed by TEM in these samples.

We have previously presented evidence of local segregation of In on (10$\underline{1}$1) planes [15]. This segregation also leads to the bending of c-planes across these fringes. The (10$\underline{1}$1) planes are polar, with six equivalent planes equally inclined to c-plane (about 62°). This is a plane on which V-defects (pinholes) in InGaN [19] are formed, and Northrup [20] has predicted In segregation. However, the angle between c-axis and the black/white fringes appears almost two times smaller. This can be related to the fact that the black and white fringe alternate in composition. Since different elements tend to segregate on different crystallographic planes, we would expect the

change of fringe orientation in black (Ga-rich) and white fringe (In-rich). Since the modulation period is so small (45Å-66Å as measured by TEM), an average direction of fringes should be deviated from (10$\underline{1}$1) planes on which In starts to segregate to satisfy planes on which Ga would segregate. Some deviations can be also introduced by structural defects (dislocations, grain boundaries and inversion domains) due to the presence of local strain. We also consider that non uniform In and Ga fluxes coupled to the sample rotation may be a factor in determining the period.

Conclusions

In conclusion, we have shown that InGaN samples grown by MBE on the AlN (or GaN) buffer layers at 530°C-580°C show periodic compositional modulation which leads to extra electron diffraction spots and XRD satellite peaks. The period of ordering increases with higher In content from $\Delta = 45$Å to $\Delta = 66$Å measured by TEM and confirmed by XRD ($\Delta = 47$Å to $\Delta = 58$Å). Samples grown on GaN with In composition x = 0.34 did not show any ordering. It is most likely that this compositional modulation was strain-driven since samples with lower mismatch to the underlying buffer layer did not show it. This study shows that it is possible to grow InGaN layers that are uniform in composition for high In content (x = 0.34) by MBE, and also the possibility to grow naturally formed thin layers on nanometer scale

Acknowledgments

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Figure captions:

Fig. 1. (a) TEM micrograph from the small area of the $In_xGa_{1-x}N$ sample with x = 0.5 sample showing black/white fringes forming tweed pattern ; (b) Photoluminescenceand absorption spectra from two samples with compositional modulation with In (78%) and Ga (22%-upper spectra and with In 50% and Ga %0 %-lower spectra.

Fig. 2 (a) Experimental diffraction patterns from the sample with x = 0.5 in [1$\underline{1}$00] projection obtained from the $In_{0.5}Ga_{0.5}N$ layer, an AlN buffer and Al_2O_3 substrate; (b) A magnified ($\underline{4}$220)$_{InGaN}$ together with AlN and the ($\underline{6}$600)substrate. Note additional diffraction spots forming small arcs around the InGaN spot with clear maxima at about 32° angle with c-axis.

Fig. 3. XRD spectra showing superlattice reflections around InGaN main reflection from the sample with x = 0.78.

Fig. 4. (a) Z contrast imaging from the sample with x = 0.5. White fringes indicate heavier element (In); Low-loss spectra (a plasmon peak) from the sample with x = 0.5: (b) from white fringe visible on Z-contrast imaging, and (c) on black fringe. Note formation of additional peak at lower energy consistent with higher Ga concentration.