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Effects of Ga on the growth of InN on O-face ZnO(000 $\bar{1}$) by plasma-assisted molecular beam epitaxy

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We compare the structural properties of InN and In_{0.95}Ga_{0.05}N films grown on O-face ZnO(000 $\bar{1}$) substrates at different temperatures. The small amount of Ga results in dramatic changes in the morphology and structural properties of InN. In particular, inversion domains start to appear at higher temperatures in the In_{0.95}Ga_{0.05}N film. This process is a consequence of the chemical reaction of ZnO with Ga which can be prevented by choosing the substrate temperature to be 450 °C or below. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4739941>]

The luminous efficacy of (In,Ga)N-based light-emitting diodes is known to decrease towards longer wavelength, resulting in what is commonly called “the green gap.”^{1,2} Different interpretations of this effect have been forwarded, but a conclusive picture has not yet emerged.^{3–6} What is generally acknowledged is the gradual degradation in crystal quality with increasing In content, an effect triggered by the immiscibility of (In,Ga)N and aggravated by the lack of native substrates, and the consequentially high density of structural defects.^{7,8}

In this context, ZnO seems to be an attractive substrate material as it is isomorphic to GaN and lattice matched to In_{0.2}Ga_{0.8}N. In contrast to GaN, it is commercially available in the form of single-crystalline 2" wafers. Yet, the growth of (In,Ga)N on ZnO was so far met with very limited success. As the primary reason for the high defect densities observed despite nominal lattice matching, several researchers identified the high chemical reactivity of the group-III metals with ZnO which results in a severe degradation of the interface between these two materials.^{9–12}

We have recently found that within a narrow temperature range, InN films of comparatively high structural quality can be synthesized on O-face ZnO(000 $\bar{1}$) despite the large lattice mismatch between these two materials.¹¹ To investigate if such a growth window also exists when adding Ga, we compare the structural properties of thin InN and In_{0.95}Ga_{0.05}N films directly grown on ZnO(000 $\bar{1}$) at different substrate temperatures. This polarity was chosen as the resulting N-polar InN films exhibit a higher morphological and structural quality than their In-polar counterparts.¹³

The InN and In_{0.95}Ga_{0.05}N films under investigation were directly grown on O-face ZnO(000 $\bar{1}$) substrates in a molecular beam epitaxy (MBE) growth chamber equipped with standard effusion cells for In and Ga and a radio-frequency plasma source for the active N species. The base pressure of the growth chamber is $<10^{-10}$ Torr, and the

chamber was maintained at $\approx 5 \times 10^{-6}$ Torr during growth. The substrate temperature T_S was varied between 400 and 500 °C. The InN films were grown with a slight N excess employing a flux ratio of In/N ≈ 0.85 . For the In_{0.95}Ga_{0.05}N films, we provided an additional Ga flux with Ga/In ≈ 0.05 . The nominal thickness of the films is about 150 nm. The morphology of the films was monitored *in situ* by reflection high energy electron diffraction (RHEED). The structural properties of the films were evaluated by x-ray diffraction (XRD) ω scans, and their microstructure was studied by transmission electron microscopy (TEM). Cross-sectional samples for TEM were prepared by plan-parallel mechanical polishing down to a sample thickness of about 10 μ m followed by ion milling with a Gatan Pips under liquid nitrogen cooling. TEM was performed in an aberration corrected FEI TITAN 80-300 using imaging conditions ($C_s < 2 \mu$ m, Gaussian focus) providing for amplitude contrast.

Figure 1 presents the RHEED patterns of the InN and In_{0.95}Ga_{0.05}N films after growth. With increasing growth temperature, the morphology of the InN films [Figs. 1(a)–1(c)] progressively improves as evidenced by the superimposed transmission and reflection pattern at 400 °C [Fig. 1(a)] and the pure reflection pattern with a well-defined specular spot and pronounced Kikuchi lines at 500 °C [Fig. 1(c)]. The underlying surface smoothing has been confirmed by atomic force microscopy (AFM) which reveals an atomically stepped surface with a root-mean-square roughness below 1 nm at 500 °C.¹¹

FIG. 1. RHEED patterns of (a)–(c) InN and (d)–(f) In_{0.95}Ga_{0.05}N films grown at three different T_S . The RHEED patterns were taken along the $\langle 11\bar{2}0 \rangle$ azimuth after growth.

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FIG. 2. FWHM of (a) 0002 and (b) $10\bar{1}2$ XRD ω scans for the InN and $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ films grown at different growth temperatures T_s . The lines are guides to the eye.

The morphology of the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ films as shown in Figs. 1(d)–1(f) is also seen to improve with increasing T_s , but to a lesser degree when compared to the case of InN. In fact, a superimposed transmission pattern is observed even at 500 °C [Fig. 1(f)]. Furthermore, the transmission pattern is more pronounced when compared to the case of pure InN. We have once again used AFM to confirm that the RHEED patterns indeed reflect the actual morphology of the respective surfaces. The addition of a mere 5% of Ga thus degrades the surface morphology significantly. We note that this effect is not caused by the low diffusivity of Ga adatoms at the low substrate temperatures used in our experiment since it can be avoided by inserting a 10 nm thick InN buffer layer between $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ and ZnO. As we will see below, the surface roughening ultimately results from a reaction between Ga and ZnO which induce a specific interface configuration.

We now turn to the structural properties of the InN and $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ films and discuss first the results of XRD ω scans in symmetric and quasi-symmetric (skew) geometry across the on-axis 0002 and off-axis $10\bar{1}2$ reflections, respectively. Figures 2(a) and 2(b) show the corresponding full-width-at-half-maxima (FWHM) as a function of the substrate temperature of the films. For the InN films (Fig. 2, squares), the FWHM of the on-axis scans are evidently quite narrow with that of the sample grown at 500 °C actually approaching the value for the substrate (25 arcsec). In contrast, the off-axis scans are very broad (≈ 2500 arcsec) regardless of sub-

strate temperature. Considering the different contributions of threading dislocations (TDs) with a - and c -component having Burgers vectors $\mathbf{b}$ of $\langle 11\bar{2}0 \rangle/3$ and $\langle 0001 \rangle$ to the FWHM of 0002 and $10\bar{1}2$ XRD ω scans,¹⁴ respectively, the observed results imply that the majority of TDs in the thin InN films are of a -type.

The addition of 5% Ga to InN changes this characteristics (Fig. 2, circles): the FWHM of the on-axis scans is significantly larger, while those of the off-axis scans is noticeably lower. A minimum for both on-axis and off-axis reflections is seen for the intermediate growth temperature of 450 °C. This result implies that the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ films exhibit a higher and lower density of a - and c -type TDs, respectively, compared to the InN films.

Cross-sectional TEM is used to study the actual nature of the structural defects in the InN and $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ films. The Burgers vector $\mathbf{b}$ of the TDs are determined by adjusting the diffraction vector $\mathbf{g}$ using the $\mathbf{g} \cdot \mathbf{b} = 0$ criterion. To distinguish TDs of a - and c -type, we use $g = 1\bar{1}00$ and $g = 0002$, respectively. Note that mixed-type TDs [i.e., those of $(a + c)$ -type] are visible in both diffraction conditions.

Figures 3(a) and 3(d) show cross-sectional TEM images of the InN film grown at 450 °C. No c -type TD is detected in the micrograph depicted in Fig. 3(a) which was acquired with $g = 0002$. In contrast, a high a -type TD density can be deduced from the micrograph shown in Fig. 3(d) recorded with $g = 1\bar{1}00$. Both of these observations are consistent with the XRD results discussed above.

The corresponding micrographs of the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 450 °C are shown in Figs. 3(b) and 3(e). Evidently, we observe a finite density of c -type TDs in Fig. 3(b) as expected from the comparatively large FWHM of the on-axis 0002 XRD ω scans (cf., Fig. 2). Likewise, a high density of TDs is detected in Fig. 3(e) as expected from the XRD results.

However, for the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 500 °C, the diffraction contrast associated to TDs is absent in Fig. 3(c); instead, a stripe-like contrast extending from the interface to the surface of the film is observed. The identification of the underlying structural defect requires a more detailed investigation.

Figure 4 displays an atomically resolved lattice image taken in a thin area of this sample. Since cations and anions

FIG. 3. Two-beam dark-field cross-sectional TEM images of an InN film grown at 450 °C [(a) and (d)], of an $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 450 °C [(b) and (e)], and of an $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 500 °C [(c) and (f)] near the $\langle 11\bar{2}0 \rangle$ zone axis with $g = 0002$ [(a)–(c)] and $g = 1\bar{1}00$ [(d)–(f)]. The arrows in (c) indicate some of the inversion domain boundaries.

FIG. 4. Atomically resolved lattice image taken in a thin sample area of the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 500°C . Two domains with opposite polarities are clearly seen. The dashed rectangle indicates the region of an inversion domain boundary.

are resolved in this micrograph, the magnified insets directly visualize the opposite polarity of the left and right parts of this image. The two domains of opposite polarity are separated by an inversion domain boundary (IDB) highlighted by the dotted rectangle. IDBs formed by adjacent domains of opposite polarity appear as contrast inversion in dark-field images taken with the noncentrosymmetric reflection $g=0002$,¹⁵ consistent with the results for this sample depicted in Fig. 3(c).

The FWHM of XRD ω scans should also be affected by these IDBs. Indeed, $10\bar{1}5$ reciprocal space maps (not shown here) indicate a reduced lateral coherence length which is very likely caused by the high density of IDBs.¹⁶ The interpretation of the FWHM displayed in Fig. 2 is thus not straightforward for this sample.

In order to identify the origin of the IDBs observed at high growth temperatures, we perform high-resolution TEM of the interface region as shown in Fig. 5. The arrow in the upper part of the image indicates an IDB. Distortions at the interface due to the high density of misfit dislocations at the interface make it difficult to discern whether or not the IDB actually originates directly at the interface. For further discussing this issue, it is important to note that we have never observed IDs for pure InN films ($350^\circ\text{C} < T_S < 600^\circ\text{C}$) and for $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ films ($T_S < 450^\circ\text{C}$). It is thus clear that Ga induces the cation-polarity of the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film on O-polar ZnO at high temperature. In fact, a mixed polarity of (In,Ga)N films grown on O-face ZnO at $T_S > 500^\circ\text{C}$ was also observed by Namkoong *et al.*,¹⁷ and Ga-polar GaN on O-polar ZnO has been reported by Ohgaki.¹² A likely reason

FIG. 5. High-resolution TEM image of the interface between the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 500°C and an O-polar ZnO substrate. The arrow indicates an inversion domain boundary. The triangles highlight the interface between $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ and ZnO.

FIG. 6. High-resolution TEM image of the interface between an $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 450°C and O-polar ZnO substrate. Misfit dislocations at the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}/\text{ZnO}$ are indicated by arrows. A 60° a -type misfit dislocation is clearly seen in the magnified inset.

for this phenomenon is the formation of a centrosymmetric crystal at the interface such as Ga_2O_3 or ZnGa_2O_4 . Ohgaki,¹² for example, argued that an atomically thin Ga_2O_3 interfacial layer may cause polarity inversion. Indeed, Ga_2O_3 and ZnGa_2O_4 crystals are detected by TEM (Ref. 18) and XRD (Ref. 9) in GaN grown on ZnO at high temperatures ($> 600^\circ\text{C}$), respectively.

These interfacial reactions between (In,Ga)N and ZnO can, however, be prevented by choosing a lower substrate temperature. Figure 6 displays the interface between an $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film grown at 450°C and the ZnO substrate. The interface is abrupt and reveals a regular misfit dislocation network, formed by 60° a -type dislocations similar to that of pure InN grown on O-polar ZnO. A well-defined interface can thus be retained for substrate temperatures up to 450°C .

In summary and conclusion, we have studied the effects of an additional Ga flux ($\text{Ga}/\text{In} \approx 0.05$) on the properties of InN films on O-face ZnO(0001) at different substrate temperatures. This small amount of Ga results in dramatic changes in the morphology and structural properties of InN. In particular, IDBs start to appear at higher temperatures in the $\text{In}_{0.95}\text{Ga}_{0.05}\text{N}$ film which we identify to result from the chemical reaction of ZnO with Ga. For obtaining high quality (In,Ga)N/ZnO, it is, therefore, imperative to avoid the formation of interfacial layers by using low substrate temperatures or by depositing a very thin coherent InN buffer layer between (In,Ga)N and ZnO.

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