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Native defects and their effects on properties of sputtered InN films

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The concept of defect chemistry is applied to investigate the native defects in the InN films prepared by radio frequency magnetron sputtering. Growth temperature and pressure ranged from 150 to 300 °C and from 0.005 to 0.07 torr, respectively, for the purpose of changing the defects and the related properties. InN is expected to form Frenkel defects, indium vacancies, and interstitials. Other major defects for the nitrogen-rich InN films include nitrogen-on-indium antisites and nitrogen interstitials at higher nitrogen pressure, as supported by the results of x-ray photoelectron spectroscopy. Structure, composition, and electrical properties coincide with defect types and density. © 2008 American Institute of Physics. [DOI: 10.1063/1.3003865]

Indium nitride (InN) with a direct band gap from ~ 0.9 to ~ 0.7 eV has enormous applications in optoelectric devices such as solar cells, light-emitting diodes, and laser diodes after combining with GaN to form InGaN alloys, having band gaps spanning the spectrum from infrared to ultraviolet.^{1,2} The major debates now for InN have been the origin of its invariably *n*-type conductivity and its defect type.

The Kröger-Vink notation has been developed to describe the defects in an ionic compound.³ There are three parts in this notation: the main body representing a vacancy or ion, the subscript part for host lattice site or interstitial, and the superscript part for the relative charge. The unintentional *n*-type conductivity of InN has long been assumed to be due to nitrogen vacancies $(V_N^{\cdot \cdot})$, oxygen (O_N^{\cdot}) and silicon (Si_{In}) impurities, or interstitial hydrogen (H_i) .⁴⁻⁶ In this report, the relative charges on the superscript part are added to the above defects. Positron annihilation measurements have been conducted on epitaxial InN films to identify In vacancies.' The major defects had been attributed to interstitial nitrogen or the combination of nitrogen-on-indium antisite defects and indium vacancies, based on the analyses of lattice dimension by x-ray diffraction (XRD) and photoelectron peaks by x-ray photoelectron spectroscopy (XPS).^{8,9}

The growth of InN has been difficult because of the low dissociation temperature and the lack of a lattice-matched substrate. High quality single-crystalline epitaxial InN films have been grown by metalorganic vapor phase epitaxy and molecular beam epitaxy (MBE).^{1,10} InN films display different band-gap values between 1.8 and 0.9 eV, which were related to the growth-dependent stoichiometry or the In/N ratio in films.^{11,12} rf sputtering produces polycrystalline InN films with high N/In ratios.⁹

To investigate the native defects and their effects on film performance, we deposited InN films by rf magnetron sputtering with an indium target at 150-300 °C and rf power of 40 W. Growth at different pressures of 0.005-0.07 torr was also conducted for the purpose of creating defects.

InN films were grown by rf magnetron sputtering in an ambient of nitrogen, with an indium target. The substrate was a single crystalline sapphire (0001) plate. The growth temperature was controlled at 150-300 °C and the growth pressure ranged from 0.005 to 0.07 torr. During the deposition, the rf sputtering power was kept constant at 40 W. The structure and the crystallinity of the films were evaluated by XRD (Rigaku D/Max-2500, Japan). A field-emission scanning electron microscope (SEM) (JEOL JSM 6500F, Japan) equipped with energy-dispersive spectroscopy was used to observe growth morphology and to analyze chemical composition. A Hall effect measurement system (HL 5500, Nanometrics Inc., USA) was used to measure the resistivity and carrier concentration. XPS (VG Scientific, UK) with an Al $K\alpha$ radiation source was used to determine the chemical bonding after a sputter etch using argon ions for 10 min.

Figure 1 shows the XRD spectra of sputtered InN films



FIG. 1. (Color online) XRD spectra of sputtered InN films deposited at (a) different substrate temperatures with a constant pressure of 0.03 torr and at (b) different growth pressures with a constant substrate temperature of 300 °C.

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FIG. 2. SEM morphologies of sputtered InN thin films deposited at different substrate temperatures of (a) 150 $^{\circ}$ C and (b) 300 $^{\circ}$ C under a constant pressure of 0.03 torr.

deposited at (a) different substrate temperatures with a constant pressure of 0.03 torr and at (b) different growth pressures with a constant substrate temperature of 300 °C. For the temperature effect [Fig. 1(a)], the InN films had a wurtzite structure. The growth orientation of InN films changed from a random orientation, the c-axis orientation, to a preferred [1011] orientation, as the growth temperature increased from 150 to 300 °C. The reason for obtaining randomly oriented grains at 150 °C is attributed to the low surface kinetic energy. As the growth temperature increased to 200 °C, InN adatoms were arranged into the orientation of the [0001] substrate. At a higher growth temperature of 300 °C, the growth of polycrystalline InN films had a preferred thermodynamically stable orientation of [1011]. For the pressure effect [Fig. 1(b)], the *c*-axis dominated orientation of the wurtzite phase occurred at low growth pressures. The preferred [1011] orientation for the 300 °C-grown InN in Fig. 1(a) changed to the *c*-axis substrate orientation at low pressure due to the larger mean free path. As the growth pressure increased, InN films had poor crystallinity. At a high pressure of 0.07 torr, a cubic phase of InN was produced.¹³

Figure 2 displays SEM morphologies of sputtered InN thin films deposited at different substrate temperatures of (a) 150 °C and (b) 300 °C under a constant pressure of 0.03 torr. The InN films were polycrystalline. The grain characteristics of InN films are related to their growth orientation revealed by XRD analysis. The randomly oriented grains had a round shape. The preferentially oriented [1011] grains had a shape of elongated pyramid.

Figure 3 shows the variations in [(a) and (d)] atomic percentage, [(b) and (e)] lattice dimension, and [(c) and (f)] resistivity and carrier concentration of sputtered InN films deposited at [(a)-(c)] different substrate temperatures with a constant pressure of 0.03 torr and at [(d)-(f)] different growth pressures with a constant substrate temperature of $300 \,^{\circ}$ C. From the composition analysis in Figs. 3(a) and 3(d), InN films were nitrogen rich and had a N/In ratio of \sim 1.9. At a higher pressure of 0.07 torr, the ratio increased to 2.35. Lattice dimension changed with process condition, as shown in Figs. 3(b) and 3(e). The lattice constants a and c changed in the opposite way at different growth temperatures in Fig. 3(b). The lattice dimension expanded a lot at the pressure of 0.07 torr due to a phase change [Fig. 3(e)]. The resistivity decreased with the growth temperature but increased with growth pressure [Figs. 3(c) and 3(f)]. The carrier concentration did not have an apparent change with temperature [Fig. 3(c)], but it slightly decreased with growth pressure [Fig. 3(f)]. Hydrostatic strain, based on the slope of lattice constants a and c, was observed in the sputtered InN This a films. Our sputtered InN films were not totally under the



FIG. 3. (Color online) The variations in [(a) and (d)] atomic percentage, [(b) and (e)] lattice dimension, and [(c) and (f)] resistivity and carrier concentration of sputtered InN films deposited at [(a)–(c)] different substrate temperatures with a constant pressure of 0.03 torr and at [(d)–(f)] different growth pressures with a constant substrate temperature of 300 °C.

state of hydrostatic strain, as shown in Figs. 3(b) and 3(e).

The possible positively charged intrinsic defects in InN include $V_N^{,..}$, $In_i^{,..}$, and $N_{In}^{,..}$. The possible negatively charged intrinsic defects include $N_i^{,..}$ and $V_{In}^{,..}$. The indium-on-nitrogen defects cannot occur because the nitrogen site is too small for indium to occupy. Based on the facts of (i) nitrogen-rich composition, (ii) the existing defects of $N_{In}^{,..}$ antisites and $N_i^{,..}$ interstitials proposed by Butcher *et al.*,^{8,9} (iii) larger lattice expansion at higher pressure of 0.07 torr, and (iv) the higher resistivity at higher growth pressure, the defect-formation equations are formulated as given below.

Case 1. Under low nitrogen pressure,

$$In_{In} = In_i^{\prime\prime\prime} + V_{In}^{\prime\prime\prime}, \tag{1}$$

$$V_{\text{In}}^{\prime\prime\prime} + 1/2N_2 = N_{\text{In}}^{..} + 5e', \qquad (2)$$

$$In_{In} + 1/2N_2 = In_i^{...} + N_{In}^{...} + 5e'.$$
(3)

Case 2. Under high nitrogen pressure,

$$In_{In} = In_i^{\dots} + V_{In}^{\prime\prime\prime}, \tag{4}$$

$$V_{In}^{\prime\prime\prime} + N_2 = N_{In}^{\cdot\cdot} + N_i^{\prime\prime\prime} + 2e^{\prime}, \qquad (5)$$

$$In_{In} + N_2 = In_i^{...} + N_{In}^{...} + N_i^{'''} + 2e'.$$
(6)

The above equations need to satisfy the balances of mass, lattice site, and electrical charge. To realize the *n*-type conduction for InN, the overall defect equations need to have net electrons. The major assumption in formulating the defect equation is the formation of intrinsic Frenkel defects [Eqs. (1) and (4)]. As a good comparison to InN, the wurtzite ZnO also prefers to form Frenkel defects of V_0^{-} and O_1'' from the larger oxygen anions.³ The consideration of larger In³⁺ cations in InN to form Frenkel defects of In_i⁻⁻⁻ and V_{In}'' is reasonable. The *in situ* formed indium vacancies [Eqs. (1) and (4)] are occupied by nitrogen coming from the growth atmosuble sphere, and hence N_{inc}^{-} antisites defects are generated [Eqs. (1) P



FIG. 4. (Color online) The variations in the N 1s XPS spectra with the growth pressures of (a) 0.008 torr and (b) 0.03 torr for sputtered InN films.

(2) and (5)]. Once many vacancies are occupied, nitrogen from the higher growth pressure can enter interstitial sites to form N_i''' defects [Eq. (6)]. Under the higher nitrogen pressure, it is expected that the resistivity of InN films will increase [Fig. 3(f)] due to the decrease in electron concentration [Eqs. (3)–(6)]. The reason for the *in situ* defect formation is expectedly related to the low defect-formation energy (2.5 eV for ZnO *versus* 1.1 eV for AgCl).

Figure 4 shows the variations in the N 1*s* XPS spectra with the growth pressures of (a) 0.008 torr and (b) 0.03 torr for sputtered InN films. The N 1*s* core level photoelectron peaks are of interest here since any peak not related to In–N bonding indicates the nitrogen-related defects. The XPS peaks were deconvoluted using the VENDOR software. The peaks at ~396.0 eV in Figs. 4(a) and 4(b) have been attributed to In–N species. The peak at ~398.0 eV, existing in all different growth conditions, is contributed to the nitrogen-on-indium antisites (N_{In}[•]). At a higher pressure of 0.03 torr, the generation of a third broad peak at ~400.9 eV in Fig. 4(b) can be attributed to the interstitial nitrogen (N_I^{'''}). The peak at ~400 eV had been attributed to the interstitial nitrogen in the N-doped TiO₂ powder.¹⁴

The change in material property with process parameter is related to defects. The existing defects in nitrogen-rich InN films including $In_i^{,..}$, $V_{In}^{,..}$, $N_{In}^{,..}$, and $N_i^{,..}$ have their own equilibrium ratio at different process conditions. With the aid of XPS, the InN films deposited at 300 °C and 0.03 torr showed the existence of nitrogen interstitials, which should lead to lower electron concentration as predicted by Eq. (6). The resistivity of 300 °C-grown films is shown in Fig. 3(c). InN deposited at lower temperatures with higher resistivity should have fewer electrons or more nitrogen interstitials. With more nitrogen interstitials, the InN films have relatively smaller *c* and larger *a* lattice values [Fig. 3(b)] as a result of the stress compensation between tension and compression arising from the vacancies and interstitials. For the effect of growth pressure, the InN films deposited at 300 °C and 0.008 torr did not show N_i''' [Fig. 4(a)], which should lead to higher electron concentration [Eq. (3)]. At pressures lower than 0.008 torr, InN films did not have N_i''' and resistivity remained low. At a higher pressure of 0.07 torr, many Ni''' defects were produced and the resistivity was higher [Fig. 3(f)]. However, the InN film produced at 0.07 torr had a high N/In ratio of 2.35 [Fig. 3(d)] and favored the formation of a new cubic phase for the purpose of stress release [Fig. 1(b)].

In summary, InN films were fabricated at 150–300 °C with growth pressures of 0.005–0.07 torr by rf magnetron sputtering. InN films were nitrogen rich. At a higher growth pressure of 0.03 torr, the defect of nitrogen interstitials was observed by XPS. At pressures below 0.03 torr, the nitrogen-on-indium antisites were the major defects. Supported by the observed defects, the defect-formation equations were formulated. The existing defects in nitrogen-rich InN films include $In_i^{...}, V_{In}^{''}, n_{in}^{...}$ and $N_i^{'''}$ with $N_{In}^{...}$ and $N_i^{'''}$ as the major defects. Electrical resistivity, which is higher at higher defect concentration of nitrogen interstitials, can be predicted from the defect-formation equations.

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