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# Room-temperature heteroepitaxy of single-phase $Al_{1-x}In_xN$ films with full composition range on isostructural wurtzite templates

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ABSTRACT

$Al_{1-x}In_xN$ heteroepitaxial layers covering the full composition range have been realized by magnetron sputter epitaxy on basal-plane AlN, GaN, and ZnO templates at room temperature (RT). Both $Al_{1-x}In_xN$ single layers and multilayers grown on these isostructural templates show single phase, single crystal wurtzite structure. Even at large lattice mismatch between the film and the template, for instance InN/AlN (~13% mismatch), heteroepitaxy is achieved. However, RT-grown $Al_{1-x}In_xN$ films directly deposited on non-isostructural *c*-plane sapphire substrate exhibit a polycrystalline structure for all compositions, suggesting that substrate surface structure is important for guiding the initial nucleation. Degradation of $Al_{1-x}In_xN$ structural quality with increasing indium content is attributed to the formation of more point- and structural defects. The defects result in a prominent hydrostatic tensile stress component, in addition to the biaxial stress component introduced by lattice mismatch, in all RT-grown $Al_{1-x}In_xN$ films. These effects are reflected in the measured in-plane and out-of-plane strains. The effect of hydrostatic stress is negligible compared to the effects of lattice mismatch in high-temperature grown AlN layers thanks to their low amount of defects. We found that Vegard's rule is applicable to determine *x* in the RT-grown $Al_{1-x}In_xN$ epilayers if the lattice constants of RT-sputtered AlN and InN films are used instead of those of the strain-free bulk materials.


## 1. Introduction

Since the bandgap of InN was revised to be in the infrared (IR) region (~0.7 eV) [1–6], $Al_{1-x}In_xN$ alloys have become very important semiconductors due to their wide bandgap range, covering deep ultraviolet (UV) to IR. Hence, most of the semiconductor optoelectronics can possibly be fabricated from $Al_{1-x}In_xN$ alloys, such as deep-UV laser diodes, infrared laser diodes, solar cells, high electron mobility transistors, and solar-blinded photodetectors [7–14]. However, a wide-range composition immiscibility of the $Al_{1-x}In_xN$, in the range $0.1<x<0.9$, impedes the fabrication of high-quality devices [15–18]. Phase separation of $Al_{1-x}In_xN$ in the indium-rich region may occur when the growth temperature is higher than the InN dissociation temperature of 550 °C [1–4]. Besides, high temperature growth causes strong thermal stress in epitaxial films. Because of the mismatch of thermal expansion coefficient between the film and the substrate, the in-plane strain of the epitaxial film can be changed from tensile to compressive during the cooling process, resulting in the formation of defects, cracks, and film peel off [19–21]. To suppress phase separation and eliminate thermal stress, films grown at room temperature (RT) are expected to eliminate these handicaps. Nevertheless, low growth temperature usually yields low crystalline quality of the films due to low mobility of adatoms. To overcome this disadvantage, the use of low-energy ion-assistance during epitaxial growth can be adopted to enhance the surface diffusion of adatoms [22–26]. Therefore, magnetron sputter epitaxy (MSE) [15,16,22] is a promising method for growing high-quality $Al_{1-x}In_xN$ alloys of any composition at very low temperatures thanks to its inherent possibility of utilizing a high flux low-energy ion-assistance.

Although RT-grown AlN epilayers have been demonstrated on different substrates, such as SiC and ZnO, by pulsed laser deposition and pulsed magnetron sputter deposition recently [23–25], RT-grown $Al_{1-x}In_xN$ alloys covering the full composition range have not been explored. It is not sufficient to be limited to AlN as the choice of materials for many kinds of electronics. GaN and its ternaries are an option [27], but introduce additional difficulties in controlling the MSE process due to the low melting point of gallium. Hence, development of single-crystal $Al_{1-x}In_xN$ ($0 \le x \le 1$) semiconductors is critical to explore more applications. However, growth of high-quality ternary $Al_{1-x}In_xN$ is more difficult than the binary compounds since InN and AlN have a large lattice mismatch of ~13%, which is believed to be the

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reason for the wide solid miscibility gap. Therefore, defects can more easily be generated if adatoms do not occupy the host lattice points. Moreover, the lack of proper lattice-matched substrates also results in the formation of structural defects. The defects create a higher background carrier density and act as trapping centers in the epilayers, which may impede the fabrication of high-performance devices.

In this article, we report a study on single-phase 0002-oriented wurtzite $Al_{1-x}In_xN$ ($0 \leq x \leq 1$) single layers and multilayers epitaxially grown on isostructural substrates at RT by MSE. From an application point of view, we believe that the potential of fabricating high-performance opto-electronics using low-dislocation-density AlN, GaN, and ZnO substrates (commercialized availably) at RT is very high. Growing metastable $Al_{1-x}In_xN$ onto temperature sensitive substrates, e.g., indium–tin–oxide glass, plastic, etc., by inserting a high quality seed layer is also desirable, which will vastly expand possible applications of group III-nitride semiconductors. For the fundamental physics viewpoint, investigation of the RT-heteroepitaxy using isostructural and non-isostructural substrates clarifies that substrate surface structure plays a vital role for the initial nucleation and film growth. Epitaxial film can be grown on isostructural substrates even with a large lattice mismatch between the film and the substrate. Through reducing lattice mismatch using a designed composition-graded multilayer, the quality of the as-grown film can be further increased. Deviations of lattice parameters induced by strains and increase of structural mosaicity in the epilayers, as detected by high-resolution X-ray diffraction (HRXRD), are due to the formation of point defects and extended defects which are confirmed by high-resolution transmission electron microscopy (HRTEM), and scanning TEM ((S)TEM). Moreover, the applicability of Vegard's rule for these compounds is confirmed.

## 2. Experimental details

An ultra-high-vacuum (UHV) MSE deposition chamber equipped with two 50 mm-diameter and two 75 mm-diameter targets was utilized to grow $Al_{1-x}In_xN$ alloys [15–17]. The chamber was evacuated to a base pressure of $<4\times10^{-7}$ Pa with a combination of turbomolecular and mechanical pumps. High-purity 75 mm-diameter aluminum (99.999%) and 50 mm-diameter indium (99.999%) targets were used to either co-sputter ternary $Al_{1-x}In_xN$ or sputter binary AlN and InN films under pure nitrogen ambient, supplied as pure nitrogen gas (99.999999%) achieved through a getter purifier. The substrates, including *c*-plane sapphire, metal-organic chemical vapor deposition (MOCVD) grown $GaN/Al_2O_3$ and $ZnO/Al_2O_3$ templates, were degreased with trichloroethylene, acetone, and isopropanol in ultrasonic baths for 5 min each and blown dry with pure nitrogen. High-temperature (HT) $AlN/Al_2O_3$ templates (HT-AlN) were grown in-situ at 1000 °C by MSE [8]. Prior to $Al_{1-x}In_xN$ growth, the sapphire, GaN, and ZnO substrates were outgassed for 30 min at 1000, 800, and 700 °C, respectively. All $Al_{1-x}In_xN$ single layers and multilayers were grown at RT. Typical dc-magnetron powers provided for indium and aluminum targets were of 10 and 50–350 W, respectively, to control the InN mole fraction. During the sputtering process, a pulsed substrate bias with the peak-to-peak potential of −20 to +5 V was applied to the sample holder to enhance growth by low-energy ion assistance.

The as-grown samples' structures were characterized in a Philips X'pert 4-axis materials research diffractometer with a Cu lab-source. For high resolution X-ray 2θ/ω scan (HRXRD) and rocking curve (XRC) measurement, the beam of pure Cu $k_{\alpha1}$ ($\lambda=0.15406$ nm) radiation, produced through a parabolically curved graded multilayer mirror followed by a 2-bounce symmetric channel-cut Ge(220) monochromator, was used as the primary optics, and a 2-bounce asymmetric channel-cut Ge(220) analyzer was used to collect the diffracted beam. For reciprocal space mapping (RSM), a 1° slit was used to achieve high intensities in both symmetric 0002 and asymmetric $10\bar{1}5$ RSMs. The elemental compositions of the films were determined by Rutherford backscattering spectrometry (RBS) where 2.0 MeV $^4He^+$ ions were used at an incident angle of 7° off from the surface normal to avoid channeling effects in the crystalline structure [28], and back scattered $^4He^+$ ions were detected at a scattering angle of 172°. Experimental data were analyzed by using the SIMNRA code (version 6.05) [29] to determine the $Al_{1-x}In_xN$ composition. The concentration of elements as determined from $Al_{1-x}In_xN$ single layers was used to calibrate the deposition fluxes from the magnetrons at various target powers. Microstructural analyses were performed by HRTEM, selected area electron diffraction (SAED), and (S)TEM using a FEI Tecnai $G^2$ TF 20 UT operated at 200 keV. The cross sectional TEM specimens were prepared by manual grinding and low-angle ion milling until electron transparency.

Fig. 1(a) and (b) shows schematic diagrams of single layer and multilayer $Al_{1-x}In_xN$ thin films, respectively. The growth conditions are listed in Tables 1 and 2, respectively. The single-layer samples consist of single $Al_{1-x}In_xN$ films grown on HT-AlN templates, which are labeled as $Al_{0.83}In_{0.17}N$, $Al_{0.65}In_{0.35}N$, $Al_{0.45}In_{0.55}N$, $Al_{0.28}In_{0.82}N$, and InN. The multilayer (ML) samples consist of multi $Al_{1-x}In_xN$ layers with increasing indium contents, from pure AlN or $Al_{0.83}In_{0.17}N$ to pure InN, grown on substrates of sapphire, HT-AlN, GaN, and ZnO templates, in this work denoted ML-sapphire, ML-AlN, ML-GaN, and ML-ZnO, respectively. All samples were grown at RT except for a thicker 360-nm HT-AlN grown at 1000 °C, which exhibited lattice parameters equal to those of bulk AlN [20], $c_o^{AlN}=0.498$ nm and $a_o^{AlN}=0.311$ nm, as determined by RSM, and was used as a reference sample for strain determination in the seed layer. The compositions and thicknesses of the $Al_{1-x}In_xN$ films shown in Table 1 were determined by RBS and TEM, respectively. Apparently, the aluminum content increases monotonically with magnetron power enabling a compositional control. For the multilayer samples, the magnetron powers of each layer are corresponding to those of the single layers, as shown in Table 1, with the sequence of AlN to $Al_{1-x}In_xN$ multilayer to InN. Herein, the AlN layer was grown at RT.

## 3. Results and discussion

All $Al_{1-x}In_xN$ single layers show shiny surfaces and are transparent with colors changing from colorless (transparent), to orange, to brown, and to dark brown with increasing indium content, which implies the change of the energy band gaps from UV to near IR. However, the effect of point and structural defects in the $Al_{1-x}In_xN$ films can not be ruled out as a reason for the colorless to color transition owing to possible

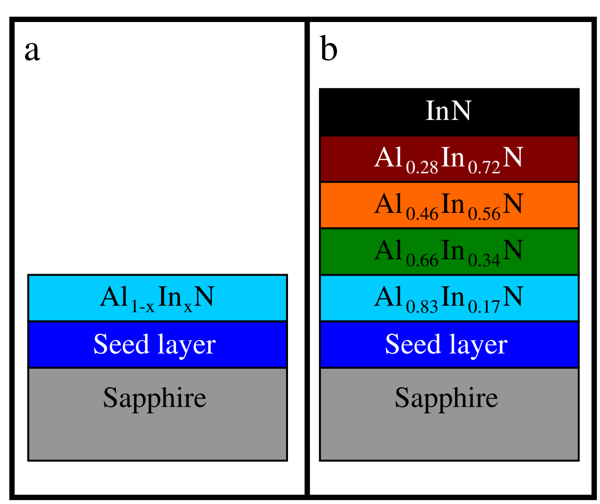


**Fig. 1.** Schematic diagrams of (a) $Al_{1-x}In_xN$ single layer grown on a template with a HT-AlN seed layer, and (b) $Al_{1-x}In_xN$ multilayer grown on different templates, HT-AlN seed layer grown by MSE, and GaN and ZnO seed layers grown by MOCVD.