Effect of nitrogen vacancies on the growth, dislocation structure, and decomposition of single crystal epitaxial (Ti$_{1-x}$Al$_x$)N$_y$ thin films

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The effect of varying nitrogen vacancies on the growth, microstructure, spinodal decomposition and hardness values of predominantly single crystal cubic phase c-(Ti$_{1-x}$Al$_x$)N$_y$ films was investigated. Epitaxial c-(Ti$_{1-x}$Al$_x$)N$_y$ films with $y = 0.67, 0.79$, and $0.92$ were grown on MgO(001) and MgO(111) substrates by magnetron sputter deposition. High N vacancy c-(Ti$_{1-x}$Al$_x$)N$_{0.67}$ films deposited on MgO(111) contained coherently oriented w-(0001) structures while segregated conical structures were observed on the films grown on MgO(001). High resolution STEM images revealed that the N-deficient growth conditions induced segregation with small compositional fluctuations that increase with the number of N vacancies. Similarly, strain map analysis of the epitaxial c-(Ti$_{1-x}$Al$_x$)N$_{0.67}$ (001) and (111) films show fluctuations in strain concentration that scales with the number of N vacancies and increases during annealing. The spinodal decomposition coarsening rate of the epitaxial c-(Ti$_{1-x}$Al$_x$)N$_y$ films was observed to increase with decreasing N vacancies. Nanindentation showed decreasing trends in hardness of the as-deposited films as the N vacancies increase. Isothermal post-anneal at 1100°C in vacuum for 120 min revealed a continuation in the increase in hardness for the film with the largest number of N vacancies ($y = 0.67$) while the hardness decreased for the films with $y = 0.79$ and 0.92. These results suggest that nitrogen-deficient depositions of c-(Ti$_{1-x}$Al$_x$)N$_{y}$ films help to promote a self-organized phase segregation, while higher N vacancies generally increase the coherency strain which delays the coarsening process and can influence the hardness at high temperatures.

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1. Introduction

Defect engineering of transition metal nitrides has attracted special attention due to the capability to tune their electronic and thermodynamic properties [1]. Cubic (Ti$_{1-x}$Al$_x$)N$_y$ is a metastable material that is widely used as protective coatings on cutting tools and industrial components because of its high hardness, wear prevention, and oxidation resistance [2-5]. In addition, a recent study shows that depending on the Al content, one can tune these coatings to have high tensile strength or high toughness which proves valuable for a variety of coating applications [5]. Another widely studied attribute of c-(Ti$_{1-x}$Al$_x$)N$_y$ is its ability to harden at elevated temperatures, an effect caused by spinodal decomposition resulting in the formation of coherent TiN-rich and AlN-rich nanometer-sized domains [6,7]. These domains have different lattice parameters [8] and elastic stiffness [9] resulting in coherency strains, which when combined effectively obstruct dislocation motion. How the decomposition can be affected and controlled have been investigated in terms of pressure [10,11], alloying [12,13], and multilayer structuring of the material [14]. The presence of point defects such as vacancies, interstitials, and anti-sites may alter the materials’ functional properties [15]. Based on the formation energy of defects in (Ti$_{1-x}$Al$_x$)N$_y$, ab initio calculations have shown that nitrogen substochiometry ($y < 1$) and superstoichiometry ($y > 1$) is due to nitrogen and metal vacancies, respectively [16], while small amounts of these vacancies have negligible

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impact on cubic to wurtzite transition [15]. Metal vacancies result in faster decomposition of c-(Ti0.24Al0.46)N0.37 arc deposited coatings has recently been reported, wherein age hardening is extended to about 1100 °C, approximately 200 °C higher than for stoichiometric coatings [20]. The age hardening ends when the decomposition proceeds by formation of wurtzite (w) AlN. The delay in w-AlN formation also improves crater wear resistance during metal machining because it suppresses diffusion of elements from the workpiece and the substrate into the coatings [21]. However, coatings grown by cathodic arc deposition contain varying density of macroparticles [22] and grain boundaries [23] that influence their functional properties [24]. Such defects also prevent detailed microstructural studies. Growth of epitaxial films on single crystal substrates overcomes these obstacles and the use of such samples may provide insight to growth mechanisms [25], microstructural features [26,27], deformation behavior [28,29], and functional properties [30,31]. Thus, synthesis of single crystal materials with tunable defect concentrations may provide fundamental and detailed information of the effect of nitrogen vacancies on the properties of (Ti1-xAlx)N films, including microstrain evolution and thermal stability.

In this study, (001)- and (111)- oriented epitaxial c-(Ti1-xAlx)N(y < 1) thin films with different N vacancy concentrations were grown using ultrahigh vacuum reactive magnetron sputter deposition. Geometric phase analysis (GPA) on high resolution high-angle annular dark-field – scanning transmission electron microscopy (HAADF-STEM) micrographs is used to gain local strain information. Differences in the population of strain concentrations of the films in their as-deposited state and during annealing at different temperatures versus nitrogen content were observed. The role of nitrogen content on the growth, defect structure, microstructure, spinodal decomposition, and functional properties of the epitaxial films is discussed.

2. Experimental Details

Cubic c-(Ti1-xAlx)N(y < 1) thin films were fabricated using an ultrahigh vacuum direct current (DC) magnetron sputtering system with a base pressure of less than 4 × 10^-7 Pa (3 × 10^-9 torr). The substrates used were MgO (001) and MgO (111) bulk crystals with >99.95% purity, which were subjected to cleaning and annealing processes prior to the deposition [32,33]. During the deposition, the substrates were held at 700°C in floating potential and continuously rotated at 14 rpm. The distance between the substrates and the targets is ~140 mm. A single element Ti (99.9% purity) target and a gas mixture of 30 sccm Ar and 10 sccm N2 were used to synthesize a 10 nm thick buffer layer. An alloy Ti3Al5N6 (99.9% purity) target was used for the deposition of the (Ti1-xAlx)N(y < 1) films. The thin TiN buffer layers were deposited to prevent the diffusion of Al from the (Ti1-xAlx)N(y < 1) films into the MgO substrate [33] since these elements are known to chemically react and form spinel at high temperatures [34]. Both targets used have a size of 50 mm in diameter. The argon flow was set to 30 sccm and the nitrogen flow was set to either 6, 8, or 10 sccm to synthesize films with different N contents. For the mentioned nitrogen flows used, the resulting overall process pressures were 2.03, 2.13 and 2.25 Pa with N2 partial pressures of 0.34, 0.45 and 0.56 Pa, respectively. The DC supplied current was set to 0.2 A and 400 V (~80 W) resulting to a deposition rate of approximately 1.25 nm/min. The films were grown to ~150 nm thickness.

The thin films were subjected to post-deposition isothermal annealing using a tube furnace with a base pressure of ~5 × 10^-4 Pa. The samples were heated at a rate of 20°C/min up to maximum temperature of either 950°C or 1100°C and held for 120 min then cooled to room temperature at a rate of 20°C/min.

X-ray diffractograms of the thin films were acquired using a PANalytical Empyrean diffractometer for crystal structure and growth orientation analysis. Symmetric and asymmetric reciprocal space maps (RSM) were recorded around MgO 111 and MgO 113, respectively. A channel-cut 2-bounce Ge(220) monochromator was used as the primary optics for the measurements. All measurements were performed using Cu Kα radiation. The equations used to compute the reciprocal lattice vectors, lattice constants, correlation length, and mosaic spread are described in detail by Calamba et al. [33].

Cross-sectional transmission electron microscope (TEM) samples were prepared either through mechanical gridding and polishing, followed by Ar-ion etching using a Gatan 691 precision ion polishing system (5 kV) or an in situ lift-out technique in a focused ion beam (FIB) - scanning electron microscope (SEM) dual beam system (Zeiss Neon 40 and FEI Helios Nanolab 650).

Morphological and microstructural information of the thin films were obtained using scanning electron microscopy (FEI Helios Nanolab 600) and aberration-corrected TEM (JEOL ARM 200F and FEI Titan™). A geometric phase analysis (GPA) script [35] added to Gatan’s Digital Micrograph was used for the scan map analysis of HAADF-STEM images. Compositional wavelengths and domain widths were measured using ImageJ software.

The atomic compositions of the thin films were measured by Rutherford backscattering spectrometry (RBS) and time-of-flight elastic recoil detection analysis (TOF-ERDA). TOF-ERDA was used to obtain the elemental distributions while RBS was used to determine the stoichiometry and thickness of the films. Both techniques employ ion beams provided by the 5 MV 15SDH-2 tandem accelerator at the Tandem Laboratory at Uppsala University. TOF-ERDA experiments were performed with a 36 MeV 127I⁷⁺ beam with a recoil angle of 45° and incident angle of 67.5° with respect to the surface normal. RBS experiments were performed with a 2 MeV 4He⁺ beam with scattering angle of 170°. The incidence angle was 5° with respect to the surface normal and a wiggling algorithm was used during acquisition to perform series of random small angle tilts on the sample and minimize channeling effects on the crystalline substrate.

The hardness values of the films were obtained by nanoindentation using a Hysitron Tribolindenter TI 950 equipped with a standard Berkovich diamond tip of 0.4 mN load resulting to 15 to 20 nm indentation depth. The area function of the tip was calibrated using a fused silica reference sample. The Oliver and Pharr method [36] was used to extract the values from the load-displacement curves and a minimum of 20 indents were made in each sample. The reported values are the average hardness and corresponding standard deviation.

3. Results

The chemical compositions of the (Ti1-xAlx)N(y < 1) thin films synthesized using different N flow rates are shown in Table 1. The resulting N2 partial fractions fN2=[N2/(N2+Ar)] for each flow rate are also listed in the table. Composition values of

<table>
<thead>
<tr>
<th>Nitrogen flow (sccm)</th>
<th>Ti (at.%)</th>
<th>Al (at.%)</th>
<th>N (at.%)</th>
<th>(Ti1-xAlx)N(y &lt; 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 sccm</td>
<td>0.25</td>
<td>18</td>
<td>34</td>
<td>(Ti0.3Al0.46)N0.37</td>
</tr>
<tr>
<td>8 sccm</td>
<td>0.21</td>
<td>22</td>
<td>34</td>
<td>(Ti0.35Al0.45)N0.32</td>
</tr>
<tr>
<td>6 sccm</td>
<td>0.17</td>
<td>26</td>
<td>34</td>
<td>(Ti0.4Al0.45)N0.27</td>
</tr>
</tbody>
</table>
x=[Al]/([Al]+[Ti]) and y=[N]/([Al]+[Ti]) were obtained using TOF-ERDA and RBS. The films contain trace impurities of C, H, and Ar. The sum of their concentration is less than 1.4 at. %. The films synthesized with N₂ partial fraction of 0.17, 0.21, and 0.25 have nitrogen content of y = 0.67, 0.79, and 0.92, respectively. As expected, the N content of the films increase when the N₂ partial fraction is increased during the deposition.

The morphologies of the as-deposited (Ti₁₋ₓAlₓ)Nᵧ thin films with average N concentration of y = 0.67, 0.79, and 0.92 are shown in Figure 1. The smoothness of the films grown on MgO(001) substrates increases with N content, while films grown on MgO(111) have a smooth appearance at y = 0.79 and 0.92. The film with y = 0.67 grown on MgO(111) shows a rough surface too. The TEM micrograph of (001)-oriented films on MgO(001) has the roughest surface among samples.

Figure 2 shows the XRD θ–2θ diffractograms of the as-deposited (Ti₁₋ₓAlₓ)Nᵧ films with an average N concentration of y = 0.67, 0.79, and 0.92 on MgO (001) and MgO(111) substrates. The (Ti₁₋ₓAlₓ)Nᵧ films with y = 0.79 and 0.92 on MgO(111) display a single peak at -37° corresponding to the 111 orientation of a cubic NaCl (B1) structure, indicating single crystal films or films with a high degree of crystallographic texture. The diffractogram of y = 0.67 film on MgO(111) contains both a 111-peak (-37°) from cubic (B1) and a 0001-peak (-36°) from wurtzite (B4). All the (Ti₁₋ₓAlₓ)Nᵧ films on MgO(001) have multiple peaks at -37° and 43° corresponding to the cubic 111 and 200 peaks, indicating that the films are not single crystalline.

Figure 3a shows the symmetric reciprocal space map (RSM) of the as-deposited c-(Ti₁₋ₓAlₓ)Nᵧ thin films with average N concentration of y = 0.67, 0.79, and 0.92 on MgO(111) substrates. The films grown on MgO(001) substrates are not single crystalline throughout the film thickness, thus RSM measurements are not applicable. The y = 0.67 sample has two distinct peaks (below and above the MgO substrate), which corresponds to the cubic and wurtzite structures. The y = 0.79 and y = 0.92 samples (Figure 3a) only have one distinct peak located above that of the substrate, indicating that the films are primarily solid solutions of c-(TiAl)N with smaller lattice parameters than the substrate. The unit-cell parameters of as-deposited y = 0.67, 0.79, and 0.92 films are c (out-of-plane, a₃) = 4.11 Å, 4.10 Å, and 4.11 Å, respectively and a (in-plane, a₂) = 4.37 Å, 4.39 Å, and 4.38 Å, respectively. Asymmetric RSM maps of (Ti₁₋ₓAlₓ)Nᵧ(111) films show a distinct reciprocal lattice point vertically displaced with respect to the spot of the substrate, which indicates a strained epitaxial layer (Figure 3b). The slight broadening of the lattice points along the omega direction signifies the presence of mosaic spread within the films. The correlation length, mosaic spread, and full width half maximum (FWHM) of the as-deposited (TiAl)N(111) films with different N contents based from the asymmetric RSM are presented in Table 2. The y = 0.79 film has the highest lateral correlation length and lowest mosaic spread and FWHM among these films, which signifies that it has the highest crystal quality. The y = 0.67 sample contains peaks from both the cubic and wurtzite structures, which could affect the asymmetric RSM measurements for lateral correlation length and mosaic spread.

Cross sectional STEM and high resolution TEM images of as-deposited c-(Ti₁₋ₓAlₓ)Nᵧ thin films with average N concentration of y = 0.92, 0.79, and 0.67 on MgO(111) substrates are shown in Figure 4. All films display a single crystal film epitaxially grown on the TiN buffer layer and MgO-substrate. The selected area electron diffraction (SAED) patterns (Figure 4a and 4b) and higher resolution TEM images (Figure 4d and 4e) of the y = 0.92 and 0.79 films confirm that they are single crystals with cubic NaCl (B1) structure. In the case of the y = 0.67 film, some regions at the top of the film contain 0001 oriented wurtzite (B4) (Figure 4c and 4f). The SAED image of the film reveals that both structures are vertically aligned, which indicates a coherent interface. Higher resolution TEM shows that the interfaces of both structures have a relationship of c-(Ti₁₋ₓAlₓ)Nᵧ(111)[1-10] with c-(Ti₁₋ₓAlₓ)Nᵧ(0001)[11-20] (Figure 4fiv).

Figure 5 shows HAADF-STEM images of epitaxial (Ti₁₋ₓAlₓ)Nᵧ thin films with average N concentration of y = 0.92, 0.79, and 0.67 on MgO(001) and MgO(111) substrates after annealing at 950°C. FFT insets indicate that all films with different N concentrations contain an epitaxial region next to the buffer layer, which is either 001 (Figure 5a to 5c) or 111 (Figure 5d to 5f) oriented along the growth direction. Epitaxial c-(Ti₁₋ₓAlₓ)Nᵧ(0001) layers are not sustained through the film thickness (Figure 5a to 5c). The y = 0.92 sample has a single crystal layer up to 20 to 40 nm thickness (marked with zigzag lines in Figure 5a) then a transition to a polycrystalline layer occurs. This transition is also observed in a stoichiometric c-(Ti₀.₃₇Al₀.₆₃)N film grown on MgO(001) [33]. The epitaxial layer of the y = 0.79 sample is thicker and grows to 80 to 120 nm before the transition to polycrystalline growth (Figure 5b). In the y = 0.67 sample grown on MgO(001) the epitaxial layer extends throughout the film thickness, however, it also contains conical features oriented in the 001 direction in some regions of the film (Figure 5c). The epitaxial c-(Ti₁₋ₓAlₓ)Nᵧ(0001) layers at different N contents also have Ti- and Al-rich domains that are elongated along the <100> directions. (Ti₁₋ₓAlₓ)Nᵧ(111) single crystals also have Ti- and Al-rich domains that are elongated along the <100> directions (Figure 5d to 5f). The wurtzite structure of the y = 0.67 film on MgO(111) in the top region of the micrograph (marked in Figure 5f) also contains elongated domains but with varying orientations.

The width of the domains in the epitaxial layers of the c-(Ti₁₋ₓAlₓ)Nᵧ(111) and c-(Ti₁₋ₓAlₓ)Nᵧ(001) films with average N concentration of y = 0.92, 0.79, and 0.67 after annealing at 950°C are shown in Figure 6. The domain size decreases with the N content of the film. The domains in the (111)-oriented film are slightly larger than in the (001)-oriented film due to a projection phenomenon.
Figure 2. XRD diffractograms of c-(Ti$_{1-x}$Al$_x$)N$_y$ (y < 1) thin films on (a) MgO (001) and (b) MgO (111) substrates with different N contents.

Figure 3. (a) Symmetric and (b) asymmetric RSM of as-deposited c-(Ti$_{1-x}$Al$_x$)N$_y$ thin films with average N concentrations of y = 0.92, 0.79, and 0.67 on MgO(111) substrates.

<table>
<thead>
<tr>
<th>Average N Concentration (y in (Ti$_{1-x}$Al$_x$)N$_y$)</th>
<th>Lateral Correlation Length (nm)</th>
<th>Mosaic Spread (˚)</th>
<th>FWHM (r.u. or Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>y = 0.92</td>
<td>815</td>
<td>0.890</td>
<td>0.010</td>
</tr>
<tr>
<td>y = 0.79</td>
<td>1311</td>
<td>0.629</td>
<td>0.007</td>
</tr>
<tr>
<td>y = 0.67</td>
<td>991</td>
<td>0.737</td>
<td>0.009</td>
</tr>
</tbody>
</table>

* Contains both cubic and wurtzite peaks

Figure 7 shows the HAADF-STEM images of the as-deposited (Ti$_{1-x}$Al$_x$)N$_{0.67}$ thin film on MgO(001) substrate and after annealing at 950°C and 1100°C. The FFT of the high-resolution images (Figure 7d and 7f) reveal that the epitaxial (Ti$_{1-x}$Al$_x$)N$_{0.67}$(001) layers remain cubic single crystals even after heat treatments. In the as-deposited state, the Ti- and Al-rich domains inside the conical features are larger than the domains in the epitaxial layer (Figure 7a). The size of the domains inside the conical features are unchanged after annealing at 950°C (Figure 7c) and have slightly grown at 1100°C (Figure 7e). At 1100°C, the domains inside the conical features are smaller than those in the epitaxial layer.

Figure 8 shows the HAADF-STEM images and the corresponding strain map of the (Ti$_{0.43}$Al$_{0.57}$)N$_{0.67}$ thin film on MgO(001) substrate annealed at 950°C. The Ti- and Al-rich domains inside the conical feature (Figure 8a) are also elongated but with varying directions. The FFT inset of the high resolution HAADF-STEM image inside the cone reveals that this region has a cubic crystal structure with its 001 direction oriented along the growth direction.
STEM with y

Figure 4. HAADF-STEM micrographs with SAED insets of as-deposited c-\(\text{Ti}_1-x\text{Al}_x\text{N}_y\) thin films with (a) \(y = 0.92\), (b) \(y = 0.79\), and (c) \(y = 0.67\) and HRTEM micrographs with FFT insets of as-deposited c-\(\text{Ti}_1-x\text{Al}_x\text{N}_y\) thin films with (d) \(y = 0.92\), (e) \(y = 0.79\), and (f) \(y = 0.67\) on MgO (111) substrates. The difference in image contrast in the STEM micrographs (darker for the upper region while brighter for the lower region) is due to the difference in the sample thickness caused by the sample preparation.

Figure 5. HAADF-STEM micrographs and FFTs of the epitaxial cubic regions of \(\text{Ti}_1-x\text{Al}_x\text{N}_y\) \((y < 1)\) thin films annealed at 950°C with N concentration of (a) \(y = 0.92\), (b) \(y = 0.79\), and (c) \(y = 0.67\) on MgO (001) substrates and (d) \(y = 0.92\), (e) \(y = 0.79\), and (f) \(y = 0.67\) on MgO(111) substrates.

\(\text{Ti}_1-x\text{Al}_x\text{N}_y\) on MgO(001) \\
\(\text{Ti}_1-x\text{Al}_x\text{N}_y\) on MgO(111)

Figure 6. Domain widths of (001)- and (111)- oriented c-\(\text{Ti}_1-x\text{Al}_x\text{N}_y\) \((y < 1)\) thin films annealed at 950°C with \(y = 0.92, 0.79,\) and 0.67.

Figure 9 displays a high magnification HAADF-STEM image where the apparent formation of a wurtzite phase is seen at the \(y = 0.92\) c-\(\text{Ti}_1-x\text{Al}_x\text{N}_y\)/c-TiN(111) film after annealing at 1100°C. Fourier transform (FFT) analysis of the HRSTEM micrograph reveals regions with domains of mixed cubic ([011] orientation) and wurtzite ([110] orientation). The observed interface between the wurtzite regions and the cubic regions appear to be irregular and shared no common interfacial habit plane, but due to the small amount of material observed it is difficult draw any conclusions.

GPA strain maps of epitaxial c-\(\text{Ti}_1-x\text{Al}_x\text{N}_y\)/c-TiN(111) and c-\(\text{Ti}_1-x\text{Al}_x\text{N}_y\)/c-TiN(001) thin films with \(y = 0.92, 0.79,\) and 0.67 are shown in Figures 10, 11 and 12. The strain maps are deduced from high-resolution HAADF-STEM images with c-TiN buffer layer as the reference. All HAADF-STEM micrographs of c-\(\text{Ti}_1-x\text{Al}_x\text{N}_y\) with different N contents display a coherent interface to the buffer layer and have composition fluctuations, indicated by the dark (Al-rich) and bright (Ti-rich) contrasts.

(Figure 8b). Figure 8a.ii details the coherency between the conical feature and the epitaxial layer. The strain map reveals a high strain concentration in the region near as well as inside the conical feature (Figure 8c).
Figure 7. HAADF-STEM and higher resolution micrographs with FFT insets of (a, b) as-deposited c-(Ti<sub>0.41</sub>Al<sub>0.59</sub>)N<sub>6</sub>(001), (c, d) annealed at 950°C and (e, f) at 1100°C.

Figure 8. (a) HAADF-STEM micrograph with FFT inset, (b) higher magnification HAADF-STEM with FFT inset, and (c) strain map of c-(Ti<sub>0.41</sub>Al<sub>0.59</sub>)N<sub>6</sub>(001) annealed at 950°C.

Figure 9. High magnification HAADF-STEM micrograph of c-(Ti<sub>0.31</sub>Al<sub>0.69</sub>)N<sub>6</sub>/c-TiN(111) showing regions with mixed cubic and wurtzite phases after annealing at 1100°C.

Figures 10(a-f) show high magnification HAADF-STEM images and corresponding in-plane GPA strain maps ($\varepsilon_{xx}$) of the as-deposited c-(Ti<sub>1-x</sub>Al<sub>x</sub>)N<sub>y</sub>/c-TiN(100) and c-(Ti<sub>1-x</sub>Al<sub>x</sub>)N<sub>y</sub>/c-TiN(111) at varying N contents after annealing at 950°C. Overall, the annealed films introduce stronger chemical fluctuations with isocrystalline coherency domains elongated along <100>-directions. At this temperature, all films have decomposed but to different degrees causing variation in the chemical compositions of the domain interfaces and sizes after annealing. The well separated domains in the films with y = 0.92 are larger with chemically more distinct interfaces compared to the domains in films with y = 0.79 and 0.67, respectively. Thus, the compositional wavelength increases with the number of N vacancies is increased (decreasing N content). The as-deposited film with y = 0.67 in the (111) direction (see Fig. 10f) showed the least sharp interfaces of compositional fluctuation among the studied films. For both (001)- and (111)-growth directions, the films with y = 0.92 in Fig. 10(a,d) and 0.79 in Fig. 10(b,e) show low homogeneous strains with minimal strain concentrations in the films. Larger and more frequent strain concentrations appear with increasing number of nitrogen vacancies up to y = 0.67, for both the (100) and (111) films ((Fig. 10(a-c) and 10(d-f), respectively). The locations of the strain concentrations are found in dispersed positions across the films. Previous work has shown that such strain concentrations are associated with dislocations caused by growth stresses [33].

Figures 11(a-f) show high magnification HAADF-STEM images and corresponding in-plane GPA strain maps ($\varepsilon_{xx}$) of the c-(Ti<sub>1-x</sub>Al<sub>x</sub>)N<sub>y</sub>/c-TiN(001) and c-(Ti<sub>1-x</sub>Al<sub>x</sub>)N<sub>y</sub>/c-TiN(111) at varying N contents after annealing at 950°C. Overall, all the annealed films introduce stronger chemical fluctuations with isocrystalline coherency domains elongated along <100>-directions. At this temperature, all films have decomposed but to different degrees causing variation in the chemical compositions of the domain interfaces and sizes after annealing. The well separated domains in the films with y = 0.92 are larger with chemically more distinct interfaces compared to the domains in films with y = 0.79 and 0.67. For all N concentrations, the number of regions with a strain concentration at 950°C is substantially higher compared to their as-
deposited states for both (001) and (111) cases. All films show that the higher strain concentrations are also found at the interface between the Ti-rich and Al-rich domains with some located in the Ti-rich domains, similar to that found in stoichiometric epitaxial c-(Ti1-xAlx)N films [33]. The inset histograms of the annealed films are generally broader than that of the as-deposited films, which indicates that there are more strain fluctuations after decomposition.

Figures 12(a-f) show high magnification HAADF-STEM images and corresponding in-plane GPA strain maps (εxx) of the c-(Ti1-xAlx)N_y/c-TiN(100) and c-(Ti1-xAlx)N_y/c-TiN(111) at varying N contents after annealing at 1100°C. In general, annealing at this temperature resulted in coarser domains and a higher number of dislocations compared to their state at 950°C. At y = 0.92 for both (100) and (111) growths, the interfaces between the Al-rich and Ti-rich domains are sharper (see Fig. 12a and 12d). The decomposed domains are also significantly larger than the domains formed at 950°C.

The hardness as a function of temperature of c-(Ti1-xAlx)N_y thin films with average N concentration of y = 0.67, 0.79, and 0.92 on MgO(001) and MgO(111) substrates are shown in Figures 13a and 13b, respectively. The hardness values of the films on both substrates show similar trends. In the as-deposited state, the hardness increases with the N content of the thin films. After annealing at 950°C, all samples have increased their hardness because of the formation of coherent domains via spinodal decomposition. Further annealing at 1100°C has caused a hardness drop for the 0.92 and 0.79 samples while hardness enhancement was still observed for the 0.67 samples. Lastly, the c-(Ti1-xAlx)N_y thin films on MgO(111) generally exhibited slightly higher hardness than the thin films on MgO(001) at all temperatures.

4. Discussion

4.1. Effect of N vacancies on growth

Composition measurements show that the films are nitrogen under-stoichiometric and the N content decreases as the N2 partial fraction decreases. In such N-deficient (Ti,Al)N_y systems (y < 1), N vacancies are known to be the dominant defect mechanism owing to its lower formation energy compared to other point defects [16]. Hence, the decreasing amount of nitrogen in the film is correlated to the increasing number of N vacancies. Composition measurements also show that Al to Ti ratio in the as-deposited films decreases slightly with increasing number of nitrogen vacancies despite originating from the same metal alloy target source. This slight variation is attributed to an increase in mixing enthalpies of AlN with decreasing N content, where more N vacancies disturb the directional chemical bonds and tend to cost more energy [37]. TiN also tends to accommodate off-stoichiometry including more N vacancies because of the metallic states’ flexibility around the Fermi level, resulting in a negative mixing enthalpy [37]. Additionally, the varying working and N2 partial pressures also cause changes in the sputtering rate of the alloyed target during reactive mode [38]. In consequence, N vacancies and N-deficient conditions slightly affects the energetics and sputter rates during growth resulting to slight variations in Ti vs Al compositions. The degree of composition difference caused by N-deficient growth conditions

Figure 10. High-resolution HAADF-STEM with FFT inset and the corresponding deformation maps εxx (in-plane strain) of as-deposited c-(Ti1-xAlx)N_y/c-TiN(111) and c-(Ti1-xAlx)N_y/c-TiN(100) thin films with (a, d) y = 0.92, (b, e) y = 0.79, and (c, f) y = 0.67. The inset histograms represent the distribution of strain values in each map.

Figure 11. (a) Schematic diagram showing the experimental setup. (b) X-ray diffractograms of c-(Ti1-xAlx)N_y films on MgO(001) and MgO(111) for various N concentrations and substrate orientations. (c, d) Raman spectra of c-(Ti1-xAlx)N_y films on MgO(001) and MgO(111) for various N concentrations and substrate orientations.
are however more significant in this study and thus will be discussed further below.

The \((\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\) \((y = 0.67, 0.79, \text{and } 0.92)\) films on MgO(001) and MgO(111) substrates with TiN buffer layers grow epitaxially to form a single crystal next to the substrate-film interface. Epitaxial growth is promoted by surface diffusion, which was obtained by applying a high substrate temperature during the depositions [39].

Epitaxial growth of c-(\(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\)(111) \(y = 0.79\) and 0.92 thin films on MgO(111) was sustained for at least 150 nm. The higher crystal quality of \(y = 0.79\) films than \(y = 0.92\) is attributed to a higher surface mobility of metal adatoms during growth in low N conditions [40]. In the case of \(y = 0.67\), epitaxial c-(\(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\)(111) was sustained in the first few atomic layers of the film but then it transitioned to formation of conical shaped \(w-(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y(0001)\) domains as the film grew thicker. This transition has also been observed for \((\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\) films with high Al content, wherein the nucleation of wurtzite phase is initiated by a small segregation of Ti and Al on the cubic growth front [41]. Similarly, in the case of \(y = 0.67\) c-(\(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\)(100), conical features with segregated Al- and Ti-rich domains are formed during growth. The tendency of N to stick to Al in medium Al and N deficient \((\text{TiAl})\text{N}\) systems has likely initiated phase segregation during growth [37]. N atoms prefer to stick to Al [37] and in such case there is a higher tendency to form a wurtzite nuclei for (111)-oriented films. Similar to the ZrAlN system [42], this tendency could have perturbed the growth of the film wherein AlN acts as sinks for Al, leading to a net diffusive flow into the precipitating segregated domains. In addition, the accumulation of lattice defects during growth due to a high vacancy concentration would then further promote nucleation of wurtzite [41]. Because of this, a segregated conical growth feature resembling the observed wedge-shaped outgrowths in nanostructured ZrAlN forms competitively from its original parent structure [42]. The competitive growth of the wurtzite phase also causes conical (wedge) shapes similarly discussed in previous studies [41]. The cubic to wurtzite phase transition also occurs in other ternary material systems containing vacancies, wherein ordering of vacancies energetically favors hexagonal phase formation in comparison to cubic [43,44].

Epitaxial growth of c-(\(\text{Ti}_{1-x}\text{Al}_x)\text{N}_y(001)\) on MgO(001) layers are not sustained throughout the film thickness, as similarly observed in a previous study of stoichiometric c-(\(\text{TiAl})\text{N}\) film on MgO(001) [33]. The transition from an epitaxial to a polycrystalline growth mode is attributed to the higher strain energy accumulating in the c-(\(\text{TiAl})\text{N}\)(001) film than the c-(\(\text{TiAl})\text{N}\)(111) film of the same chemical composition [33]. Meanwhile, cubic \((\text{Ti}_{1-x}\text{Al}_x)\text{N}_y(001)\) thin films on MgO(001) with lower N contents sustained a thicker epitaxial layer. During growth in (001) surfaces at similar temperatures, previous studies have shown that decreasing the nitrogen partial pressure \(f_{\text{N2}}\) results to a more layer-by-layer growth while increasing the \(f_{\text{N2}}\) allows growth mounds from kinetic roughening and reduced island size for nucleation [45]. This was attributed to the decrease in surface diffusivity at higher \(f_{\text{N2}}\) due to the increase in steady state N coverage [45]. In our case, the combination of the strain energy and slightly varying Al content together with the change in the diffusing species contributes to the unsustained epitaxial growth. The reduced \(f_{\text{N2}}\) allows surface diffusion to occur on MgO(001) and MgO(111) substrates with TiN buffer layers grow epitaxially to form a single crystal next to the substrate-film interface. Epitaxial growth is promoted by surface diffusion, which was obtained by applying a high substrate temperature during the depositions [39].

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resulting to prolonged epitaxial growth while higher $f_{N2}$ allows islands to easily nucleate in a polycrystalline mode.

Compositional fluctuations of elemental segregation in the as-deposited films seen in Figures 10(a-f) are expected since the intrinsic Ti and Al compositions fall under the miscibility gap [46]. Unlike the segregation observed during annealing, these local concentration fluctuations are surface-diffusion-driven [42] and highly correlated to the growth condition which is why the striped pattern is seen along their respective growth directions ($<001>$ and $<111>$). These ordered formations are driven by the minimization of the total free energy of the system under high temperature and enhanced mobility deposition conditions [26,47]. The total elastic energy of two elastically different domains [9] on the surface is reduced by creation of domain boundaries and equilibrium domain separation to the point that the interfacial energy increase is balanced out by the elastic energy relaxation [26].

The slight differences in compositional wavelengths versus N content however, are not commonly seen in previous studies of the same material. Understanding the compositional fluctuations are important because they are shown to affect the subsequent spinodal decomposition of the films [48]. This is the first experimental study to date that has observed the size changes of the compositional wavelengths in the as-deposited state due to nitrogen vacancies. These size differences can be further expounded by the changes in the energetics of the system during growth. In our case, the presence of N vacancies influence the elastic and interfacial energies but at the same time, the effect of N content on kinetic segregation affects the growing film [47]. Previous simulations of TiN growth have shown that in a nitrogen-deficient deposition condition, Ti adatoms have the thermodynamic tendency to form nitrogen-deficient (111) Ti islands because N adatoms are not present [49]. Molecular dynamics studies have also shown that

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**Figure 12.** High-resolution HAADF-STEM with FFT inset and the corresponding deformation maps $\epsilon_{xx}$ (in-plane strain) of c-(Ti$_{1-x}$Al$_x$)$_y$N$_y$/c-TiN(111) and c-(Ti$_{1-x}$Al$_x$)$_y$N$_y$/c-TiN(100) thin films with (a, d) $y = 0.92$, (b, e) $y = 0.79$, and (c, f) $y = 0.67$ annealed at 1100°C. The inset histograms represent the distribution of strain values in each map.

**Figure 13.** Hardness values of as-deposited and annealed (Ti$_{1-x}$Al$_x$)$_y$N$_y$ ($y < 1$) thin films on (a) MgO(001) and (b) MgO(111) substrates.
when N adatoms do arrive, they tend to stick to the growth front because they are kinetically hindered by the N surface migration rates being higher than N$_2$ (N adatom/N surface atom) desorption rates at the deposition temperature utilized (less than 1000 K) [50,51]. Given the high metal flux and varying levels of nitrogen-deficiency applied during growth, the degree of metal segregation is thus attributed to how the availability of incoming and adsorbed N atoms (or lack thereof) on the growing film influences the degree of Ti and Al adatoms sticking together. Fewer N atoms leads to larger nitrogen-deficient Ti and Al islands which then result to longer compositional wavelengths observed at high N vacancy concentrations. In short, the combination of the parameters used during sputter deposition together with the energetics of the material leads to these variations. The interplay between the elastic energy relaxation as well as kinetic segregation together determine the final microstructure of the film [47]. Hence, N vacancy content and nitrogen-deficient conditions promote and offers a mean to control self-organized segregation during growth.

The presence of local strains and dislocations in all as-deposited films are attributed to differences in lattice parameters and thermal expansion coefficients between film and substrate as similarly observed in previous studies [33]. In short, these are dislocations originating from growth [39,52]. However, epitaxial films with the highest N vacancy concentrations (y = 0.67) exhibited the highest local strains. This is attributed to larger differences in lattice parameter between N deficient films and substrate [53,54] as well as the increased lattice distortion caused by vacancies. In terms of growth behavior and strain concentration populations, the (100) and (111) oriented films exhibited similar trends which indicates that the orientation of the film and substrate is not a significant factor in the as-deposited state.

4.2. Effect of N vacancies on the microstructure evolution during spinodal decomposition

After annealing at 950 °C, the (Ti$_{1−x}$Al$_x$)$_\text{N}_y$ films with different N concentrations have undergone spinodal decomposition with formation of coherent domains causing more strain fluctuations. The additional strain generated originates from the lattice mismatch and elastic incompatibility of the Ti-rich and Al-rich domains [8,55,56]. Due to these elastic differences of the domains, some of the strains are relieved through misfit dislocations [33] causing strain concentrations. GPA strain maps of the films after annealing at 950 °C validate these higher strain regions, which are more pronounced and concentrated at the domain interfaces and in the Ti-rich domains. Alling et al. [37] determined that it is more energetically favorable to form stoichiometric AlN and understoichiometric TiN during decomposition by calculation of formation energies in (Ti$_{1−x}$Al$_x$)$_\text{N}_y$ for y < 1. It is also likely that higher directionality of the chemical bonding in c-AlN compared to c-TiN [9] drives c-TiN to accommodate dislocations more during segregation [33]. Thus, the tendency of the film to form understoichiometric TiN$_y$ (y < 1) during isostructural spinodal decomposition likely observed the high strain fluctuations within the coarsened Ti-rich domains. This is further corroborated by the calculations by Århammar et al. [57]. They show that Ti-N bonds are depleted (exhibited by a decrease in N p-Ti d overlap) while N p-Al p hybridization increased with increasing annealing temperature. The exact correlation of the number of N vacancies on the amount of strain concentrations, however, is a complex interplay between balancing the chemical driving force for coarsening, interfacial energy, and strain effects. An additional factor that may contribute to the complex strain distributions is the non-straight diffusion pathway of nitrogen during decomposition reported by Schramm et al. [19], wherein they experimentally observed that N prefers to be in Ti-rich domains first, followed by N returning to Al-rich domains as the system approaches a more equilibrium state. In this case the equilibrium state is pure and stoichiometric AlN and nitrogen-deficient TiN-rich domains [37]. Such a non-straight diffusion pathway is attributed to the higher diffusivity of N than Ti and Al in this system, which is amplified by the increased N vacancies in the samples [19,58]. Because of nitrogen’s complex diffusion pathway during decomposition, the strain distribution observed is also complex and cannot be directly correlated to the difference in the number of N vacancies in specific domains at this annealing temperature (950°C).

The domains of the annealed films show elongations in the elastically soft <100> directions which is in accord with what has been seen previously for annealed single crystal [33] and poly-crystalline c-(TiAl)N films [4,59]. The elongation along the elastically soft directions is related to the material’s elastic anisotropy and minimization of the stored elastic energy [6,9,60]. The domain coarsening is a measure of how far the decomposition has evolved. The coarsening is more pronounced for films with high N contents (i.e. low N vacancy concentration) similar to what has been observed in nitrogen-deficient arc deposited (Ti$_{1−x}$Al$_x$)$_\text{N}_y$ films [19]. The presence of nitrogen vacancies decreases the driving force for decomposition and lowers the decomposition rate [37], which results in smaller domains. Smaller domains, as seen for the annealed films with y < 1, are associated with more internal interfaces where the lattice is expected to be the most strained, which is also what we observe. It has been shown that for decomposed domains, a more elongated structure signifies a more elastically constrained system [53]. Thus, it is presumed that films with higher N vacancies generally increase the coherency strain.

At 1100 °C, the domain sizes of the (Ti$_{1−x}$Al$_x$)$_\text{N}_y$ films grew larger since coarsening has proceeded further. Domain coarsening is mainly driven by reduction of the interfacial energy in the system [53], while the coarsening rate is diffusion-controlled and increases with increasing temperature [59]. The sharper interfaces observed in films with y = 0.92 indicate that the chemical segregation of Ti and Al is more advanced, and the domain composition approaches pure TiN and AlN. As the domains grow larger, their interfaces become more separated and since the strain concentrations are located at the domain interfaces the dislocations also appear sparser. Moreover, in the latter stages of segregation, coarsening is primarily diffusion limited and no longer composition dependent [59] which results in fewer domain boundaries where dislocations are located, and thus explains the minimal differences in the dislocation densities between films with different amount of N vacancies (Figures 12a-f) at this higher annealing temperature (1100°C). It is also possible that the temperature is already sufficient for dislocation climb such that dislocations are annihilated and grain boundaries are formed at domain boundaries.

In addition, the y = 0.92 film deposited on MgO[111] also evidenced the formation of wurtzite domains (Figure 9) in the Al-rich regions of the film after annealing at 1100°C. This domain formation is attributed to the known tendency of c-AlN to transform into the more stable wurtzite B4 w-AlN structure when subjected to high thermal loads [23,59,61]. FFT analysis of the mixed wurtzite and cubic domains implies a relationship of (0001)$_\text{w-AlN}$/[110]$_\text{c-TiN}$ and [1120]$_\text{w-AlN}$/[110]$_\text{c-TiN}$ but we note that the spots do not exactly match their expected positions. This domain relationship has been previously observed in similar systems of ZrAlN [26] and TiAlN [62]. The relatively large size of the w-AlN domains found (> 10 nm) indicates that the growing crystallites are less constrained resulting in semicoherent wurtzite domains [56]. Considering that wurtzite phase transformations were only observed at y = 0.92 and not at y = 0.79 and 0.67 supports our notion that the state of decomposition is more advanced in films with fewer N vacancies. In this sample, the wurtzite domains are most likely at an almost-pure state, meaning high Al concentration, which is
4.3. Effect of N vacancies on the hardness values

Nanoindentation measurements show a reduction in hardness of the as-deposited \((\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\) \((y = 0.92, 0.79, \text{and} 0.67)\) films as the N content decreases, similar to what has been observed for nitrogen deficient polycrystalline c-(TiAlN) [63]. Such softening due to vacancies has also been reported in other transition metal nitride systems, such as TiN [64,65]. These studies’ argument for vacancy softening is based on a predicted change in the nature of the atomic bonding in the presence vacancies that decreases the shear modulus and thereby the hardness [64]. However, as mentioned above, others have reported vacancy hardening for the TiN and they attribute the observed vacancy hardening to pinning of dislocations at vacancies [40]. Our results show that single crystalline \((111)\)-oriented films generally have higher hardness than \((001)\)-oriented ones. Such trend is attributed to the fact that indentation along the normal of a \((111)\) surface requires plastic flow caused by slip on its secondary slip system to a larger extent than when indenting along the normal of a \((001)\) surface, which results in an increased hardness [66].

After annealed at 950°C, the hardness of the films at all N contents \((y = 0.92, 0.79, \text{and} 0.67)\) have increased because of the coherency strains generated during spinodal decomposition, which prevent propagation of dislocations during hardness measurements [67,68]. The additional dislocations generated by spinodal decomposition further acts as obstacles for dislocation motion. Some of this strain is possibly released in the films with high \(N\) \((y = 0.92, 0.79)\) contents that have formed grain boundaries when annealed at 1100°C. Such grain boundaries may annihilate some of the dislocations formed during decomposition and when combined with the strain release the net result increases the mobility of dislocation resulting in a hardness decrease. The formation of wurtzite domains (Figure 9) at 1100°C in the \(y = 0.92\) film deposited on MgO\((111)\) further explains the additional hardness reduction of the film at this temperature [69]. The relatively large and soft w-AlN domains cause loss of coherency strain that consequently lowers the hardness [7,61].

The continued increase in hardness of films with the highest vacancy composition \((y = 0.67)\) is attributed to the decreased decomposition rate caused by a weak driving force for decomposition at lower N contents. At this slower decomposition rate, the coarsening is delayed and the generated coherency strains are retained that continues to obstruct dislocation motion even after being annealed at 1100°C. Thus, the addition of nitrogen vacancies not only improves the stability of the film against coarsening but also proves to be a tool for tuning the mechanical behavior of epitaxial and single crystalline c-(Ti\(_{1-x}\)Al\(_x\))N\(_y\) films at high temperatures.

Conclusions

Nitrogen vacancy concentration was shown to have a significant effect on the growth, nanostructure and microstrain evolution during spinodal decomposition as well as mechanical properties in \((\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\) \((y<1)\) thin films. Epitaxial c-(Ti\(_{1-x}\)Al\(_x\))N\(_y\) thin films with the most vacancies \((y = 0.67)\) grown on MgO\((001)\) contained conical features with segregated domains while those grown on MgO\((111)\) substrates contained coherently oriented and conical shaped w-(0001) structures as the film grew thicker. These formations are attributed to the increasing strains and defects caused by vacancies and N’s tendency to stick to Al during growth which have perturbed the growth of the films leading to a net diffusive flow into the precipitating segregated domains. Meanwhile, the changing energetics and N-deficient growth conditions induced segregation with small compositional wavelengths in the cubic region of the films which increase with decreasing N content. Therefore, growth of \((\text{Ti}_{1-x}\text{Al}_x)\text{N}_y\) in nitrogen-deficient conditions offers a mean to promote self-organized segregation during growth.

The GPA strain maps of the epitaxial cubic regions show trends that were dependent on the differences in lattice parameters and lattice distortions in N-deficient films. During spinodal decomposition, the domain formation caused an increase in the strain fluctuation of the films while the coarsening of Ti-rich and Al-rich domains increases with N content. Nanoindentation showed a decreasing trend in hardness of the as-deposited films as the N content decreases. A continued increase in hardness of the films with the highest vacancy composition \((y = 0.67)\) even after annealing at 1100 °C was attributed to its decreased decomposition rate which retains the coherency strains in the film. Overall results show that films with more N vacancies generally increase the coherency strain, delays the coarsening process and improves the stability of single crystal c-(Ti\(_{1-x}\)Al\(_x\))N\(_y\) against coarsening.

Declaration of Competing Interest

None.

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