

Final Draft
of the original manuscript:

Schroeder, J.L.; Saha, B.; Garbrecht, M.; Schell, N.; Sands, T.D.; Birch, J.:
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metal/semiconductor superlattices**
In: Journal of Materials Science (2015) Springer

DOI: 10.1007/s10853-015-8884-5

Thermal stability of epitaxial cubic-TiN/(Al,Sc)N metal/semiconductor superlattices

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Abstract

We report on the thermal stability of epitaxial cubic-TiN/(Al,Sc)N metal/semiconductor superlattices for potential plasmonic, thermoelectric, and hard coating applications. TiN/Al_{0.72}Sc_{0.28}N superlattices were annealed at 950 °C and 1050 °C for 4, 24, and 120 hours, and the thermal stability was characterized by high-energy synchrotron-radiation based 2D x-ray diffraction, high-resolution (scanning) transmission electron microscopy (HR(S)/TEM), and energy dispersive x-ray spectroscopy (EDX) mapping. The TiN/Al_{0.72}Sc_{0.28}N superlattices were nominally stable for up to 4 hours at both 950 °C and 1050 °C. Further annealing treatments for 24 hours and 120 hours at 950 °C led to severe interdiffusion between the layers and the metastable cubic-Al_{0.72}Sc_{0.28}N layers partially transformed into cubic-Al_{0.72-x}Sc_{0.28}N and thermodynamically stable hexagonal-AlN phases with the h-AlN grains displaying two epitaxial variants with respect to c-TiN and c-Al_{0.72-x}Sc_{0.28}N. EDX mapping suggests that scandium has a higher tendency for diffusion in TiN/(Al,Sc)N than titanium or aluminum. Our results indicate that the kinetics of interdiffusion and the cubic to hexagonal phase transformation play a major role when designing TiN/(Al,Sc)N superlattices for high temperature applications.

Keywords: superlattice, thermal stability, thin films, plasmonics, thermoelectric, hard coatings

Introduction

For 30 years researchers have been pursuing epitaxial metal/semiconductor superlattices with low defect and dislocation densities for electronic, photonic, and plasmonic devices [1]. Saha et al. recently demonstrated epitaxial metal/semiconductor superlattices (i.e. TiN/Al_{0.72}Sc_{0.28}N) with low defect density [2]. The Al_{0.72}Sc_{0.28}N composition is lattice

matched to TiN and scandium alloying increases the critical thickness of the metastable c-AlN layers [3] from 2 nm to 200 nm [2]. These metal/semiconductor superlattices show potential for applications as plasmonic metamaterials [4], high-temperature thermoelectric/thermionic devices, and hard coatings for cutting tools [5]. All three of these application areas require high-temperature thermal stability of the superlattice structure. Plasmonic applications depend on thermal stability due to localized heating [6]; nitride superlattices have been investigated for high-temperature thermoelectric applications up to 1000 °C [7, 8]; and (Ti,Al)N-based hard coatings for cutting tools routinely experience 700 °C – 1000 °C operating temperatures [9, 10].

Thus, we evaluated the high temperature behavior of TiN/Al_{0.72}Sc_{0.28}N superlattices via annealing experiments and ex-situ characterization of the crystallographic and microstructural properties. The main results of this work are highlighted here:

- c-(Al,Sc)N partially phase transforms into epitaxial h-AlN grains with increased annealing time.
- TiN and (Al,Sc)N layers of the superlattice interdiffuse with increased annealing time.
- Coherent nanometer-scale h-AlN grains are distributed throughout the film thickness due to layer intermixing.

Experimental

10 nm/10 nm TiN/Al_{0.72}Sc_{0.28}N superlattices were deposited on (001)-oriented MgO substrates at 750 °C in a 10 mTorr Ar/N₂ (4 sccm Ar:6 sccm N₂) ambient via reactive dc-magnetron sputtering (PVD Products, Inc.) from scandium (99.998% purity), aluminum (99.99%), and titanium (99.99%) targets (50 mm diameter x 6 mm thick) in a top-down confocal arrangement. The base pressure was < 6.7·10⁻⁶ Pa (5.0·10⁻⁸ Torr) prior to deposition

at 750 °C. Sputtering was performed in constant power mode (Al = 200 W; Sc = 180 W; Ti = 200 W) with a target to substrate distance of 9 cm and a substrate rotation speed of 5 rpm. Superlattices were deposited by opening and closing target shutters for the alternating TiN and Al_{0.72}Sc_{0.28}N layers.

Annealing treatments were performed in a custom-designed vacuum chamber annealing furnace using a Boralectric tube heater. The vacuum chamber was evacuated to $< 6.7 \cdot 10^{-4}$ Pa ($5 \cdot 10^{-6}$ Torr) before continuously flowing 30 sccm forming gas (5% H₂:95% N₂) to achieve a pressure of 8 mTorr. The superlattices were annealed (ramp rate = 20 °C min⁻¹) at 950 °C for 4, 24, and 120 hours as well as 1050 °C for 4 and 24 hours. All annealed superlattices originated from the same deposition. Furnace and sample temperatures were confirmed with a dual wavelength pyrometer (CellaTemp PA40; 0.95 and 1.05 μm).

The thermal stability of 10 nm/10 nm TiN/Al_{0.72}Sc_{0.28}N superlattices was characterized by annealing treatments followed by synchrotron-radiation based x-ray diffraction imaging, High-resolution (scanning)/transmission electron microscopy (HR(S)/TEM), and energy dispersive x-ray spectroscopy (EDX) mapping. Synchrotron-radiation based x-ray diffraction imaging was conducted at the High Energy Materials Science beamline P07 at PETRA III, DESY (Hamburg, Germany). Figure 1e provides a schematic of the x-ray diffraction setup. X-ray diffraction was conducted in transmission mode by directing a 10 μm x 400 μm x-ray beam approximately parallel to the film surface of a 4 mm x 4 mm x 0.5 mm sample, whereby diffraction occurs throughout the illuminated superlattice volume. The beam was approximately parallel to MgO [010] and the MgO substrate was partially irradiated by the x-ray beam, but no diffraction was observed from the MgO due to intentional misalignment of the MgO with respect to the x-ray beam. The 87.1 keV high-energy x-rays resulted in small diffraction angles (2-10°) and the diffraction intensity was measured with a stationary Perkin

Elmer XRD1621 2D detector placed 2500 mm from the sample, with the resulting 2D diffraction pattern representing a slice of reciprocal space.

HR(S)/TEM and EDX mapping were obtained using the Linköping probe- and image aberration-corrected and monochromated FEI Titan³ 60–300 microscope equipped with a high brightness XFEG source and ChemiSTEM Super-X detectors. The microscope was operated at an accelerating voltage of 300 kV. All TEM images were recorded with the beam parallel to MgO [010].

Results and discussion

Synchrotron-radiation based x-ray diffraction imaging

Figure 1a-1d present 2D x-ray diffraction patterns for the as-deposited TiN/Al_{0.72}Sc_{0.28}N superlattice in addition to superlattices annealed at 950 °C for 4 hours, 24 hours, and 120 hours. The as-deposited superlattice on a (001)-oriented MgO substrate is predominantly (002)-oriented as evidenced by the dominant 002 reflection (d-spacing = 2.13 Å), which is oriented along the growth direction (Figure 1a). Corresponding diffraction peaks from the {002} family of planes are observed along the perimeter of the 002-diffraction ring. The 220 reflections originate from the same grains that produce the 002 reflections, with the location of the 220 reflections being determined by the 45° interplanar angle between the {220} and {002} planes in the cubic crystal system. Diffraction resulting from the periodicity of the superlattice is present in the form of superlattice reflections immediately below the 002 reflection from the superlattice and interference fringes in the small angle x-ray scattering (SAXS) signal.

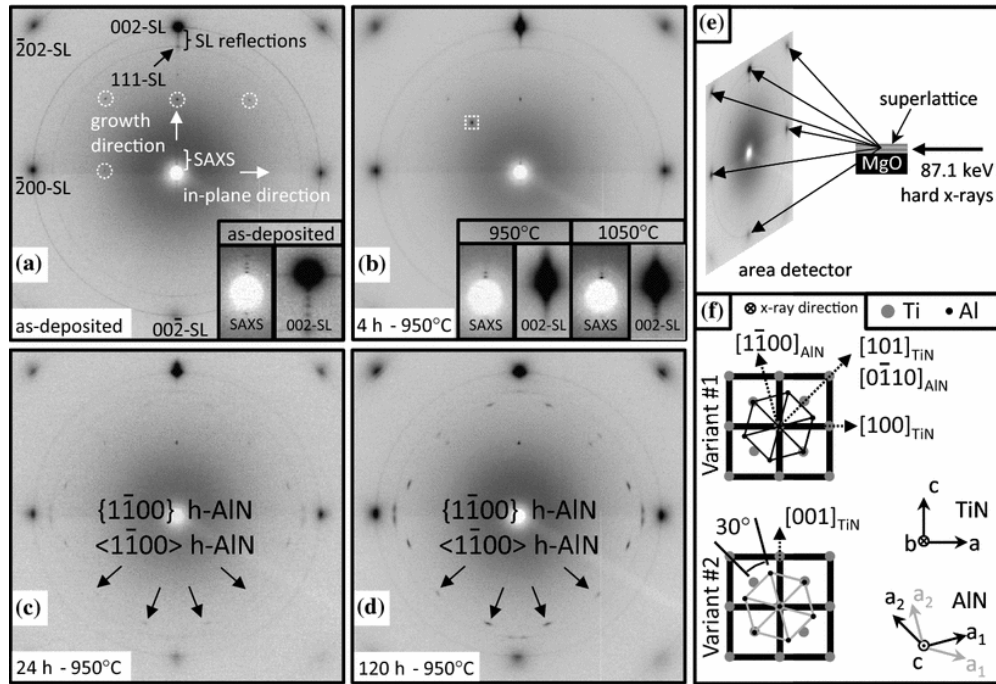


Fig. 1

a as-deposited superlattice is (002)-oriented and displays superlattice reflections and interference fringes in the SAXS signal; **b** superlattice reflections are still present after annealing for 4 h at both 950 and 1050 °C; **c** superlattice reflections have disappeared, and c-Al_{0.72}Sc_{0.28}N has begun to transform into Al-deficient (Al,Sc)N and h-AlN phases as indicated by 12 diffraction spots from two variants of h-AlN; **d** increased annealing time leads to an increased concentration of h-AlN as indicated by darker h-AlN spots; **e** schematic of synchrotron-radiation-based 2D X-ray diffraction imaging of thin films in transmission mode; **f** schematic of two epitaxial variants (offset by 30°) of h-AlN on c-TiN

Standard lab-based x-ray diffraction (not shown) indicates that the as-deposited superlattices are epitaxial with strong (002)-texture. However, the full, but weak, 002- and 111-diffraction rings in the synchrotron-radiation diffraction patterns indicate that randomly oriented grains are also present in the microstructure, albeit a small fraction based on the low relative intensity of the diffraction rings compared to the 002 reflection from the superlattice. The presence of a weak superlattice 111 reflection (d-spacing = 2.46 Å) indicates some (111)-texture. The (111)-oriented grains are presumed to originate from the initial stages of film growth and are subsequently overwhelmed by the dominant (002)-oriented grains.

Other noteworthy features in the 2D x-ray diffraction patterns are as follows: first, the single-crystal MgO substrate does not produce any appreciable diffraction signal since it is not exactly aligned with respect to the x-ray beam; second, the small diffraction spots highlighted with dashed circles are a duplicate representation of the main diffraction signal due to higher undulator x-ray beam harmonics and thus can be ignored; third, the central white spot is due to a lead beam stop which protects the detector from the high-intensity non-diffracted direct x-ray beam.

The superlattice maintains most of its diffraction features and no new additional phases are present after a 4 hour anneal at 950 °C (Figure 1b) indicating that the superlattices are nominally stable in the cubic rocksalt phase for at least 4 hours at 950 °C. The inset images of Figure 1b show close-up views of the data representing the SAXS-signal and 002 reflection from the superlattice (i.e. “002-SL”) at both 950 °C and 1050 °C. The decreasing intensity of the superlattice reflections compared to the as-deposited sample (inset images of Figure 1a) indicates a gradual loss of abruptness in the superlattice interfaces, which is explained by interdiffusion of the individual TiN and (Al,Sc)N layers, as discussed later.

We note an unidentified high intensity diffraction spot (highlighted by a dashed square) in Figure 1b. The spot corresponds to a d-spacing of 4.20 Å and is almost 45° from the surface normal. The d-spacing is closely related to the d-spacing of the 002 MgAl₂O₄ spinel planes, but we rule out the spinel structure due to the off-axis orientation, the peak not appearing at longer annealing times, and an EDX line profile analysis across the MgO/film interface showing no aluminum in the MgO substrate.

Figure 1c shows the superlattice after a 24 hour anneal at 950 °C, with three new features of interest. First, the superlattice reflections have disappeared indicating that the film

has lost its periodicity. Second, the onset of twelve equally spaced AlN $\{1\bar{1}00\}$ diffraction spots (d-spacing = 2.69 Å) indicates the formation of hexagonal-AlN that results from the cubic-Al_{0.72}Sc_{0.28}N phase losing aluminum (cubic-Al_{0.72-x}Sc_{0.28}N). Höglund et al. observed similar behavior when annealing c-(Al,Sc)N thin films [11]. The twelve diffraction spots, which are 30° apart, are due to the presence of two different h-AlN grain orientations rotated 30° with respect to each other [12]. Figure 1f schematically presents the two h-AlN variants. The epitaxial relationship between h-AlN and c-TiN is (0001)[0 $\bar{1}$ 10] AlN // (001)[101] TiN. The twelve diffraction spots originate from horizontally-oriented h-AlN grains, which are defined as h-AlN grains whose basal planes are perpendicular to the substrate surface. Vertically-oriented h-AlN grains (i.e. basal planes parallel to the substrate surface) are also present, but their AlN $\{1\bar{1}00\}$ planes do not fulfill the diffraction condition. Third, peaks have appeared along the perimeter of the 111-diffraction ring. These peaks are caused by the h-AlN (0002) d-spacing (2.49 Å), which nearly coincides with the superlattice (111) d-spacing (2.46 Å). The location of these peaks implies that the h-AlN basal planes are tilted approximately 2.5° with respect to the TiN lattice. Both Chen et al. and Deng et al. have observed similar tilting behavior of h-AlN on TiN [13,14]. The cubic-(Al,Sc)N phase continues to lose aluminum with extended annealing time as evidenced by the more prominent hexagonal-AlN diffraction spots after a 120 hour anneal at 950 °C (Figure 1d). Vertically-oriented h-AlN grains (i.e. basal planes parallel to the substrate surface) are indicated by the two faint 0002 h-AlN reflections (d-spacing = 2.49 Å) at the bottom of the image.

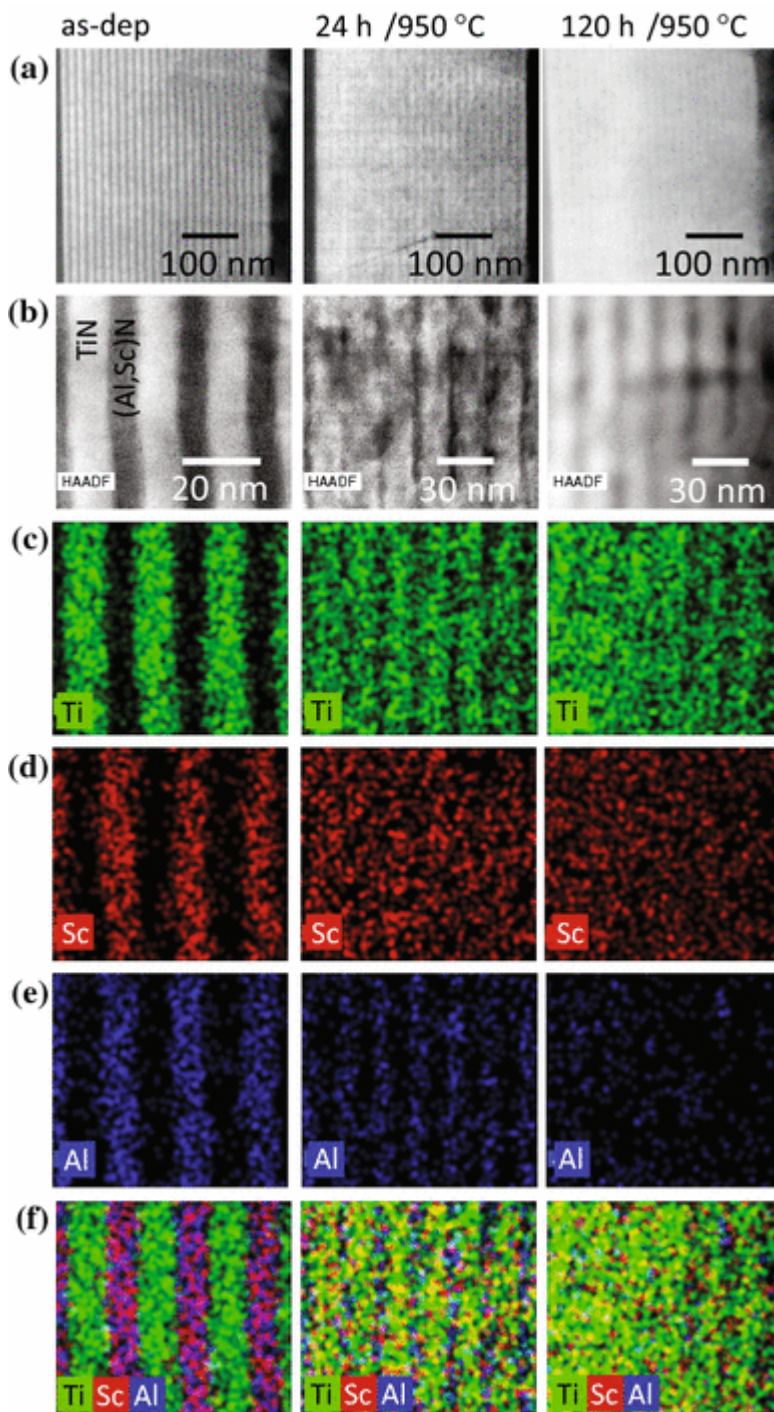


Fig. 2

(color online) Layer intermixing and loss of superlattice structure with increased annealing time confirmed with a,b (HAADF)-STEM micrographs; c–e EDX maps of titanium (Ti), scandium (Sc), and aluminum (Al); f combined elemental EDX maps

HR(S)/TEM and EDX mapping

The STEM and EDX data of Figure 2 clearly demonstrate increased intermixing of the TiN and (Al,Sc)N layers with increased annealing time. Figure 2a and 2b display high-angle annular dark field (HAADF)-STEM micrographs of the as-deposited superlattice as well as superlattices annealed for 24 hours and 120 hours at 950 °C. Individual EDX maps of titanium, scandium, and aluminum from the same area as Figure 2b are provided below each micrograph (Figure 2c, 2d, and 2e) in addition to combined EDX maps from titanium, scandium, and aluminum (Figure 2f).

The (HAADF)-STEM micrograph of the as-deposited superlattice (Figure 2b) shows distinct TiN layers (white) and (Al,Sc)N layers (gray) due to the atomic number dependence of the contrast mechanism in HAADF (Z-contrast). The corresponding EDX maps indicate that titanium is only located in the TiN layers while scandium and aluminum are only located in the (Al,Sc)N layers. After a 24 hour anneal at 950 °C the individual layers and interfaces are less distinct than the as-deposited state. The EDX maps show the onset of layer intermixing as a result of diffusion. The titanium and aluminum maps show diffuse layering compared to the as-deposited film, indicating titanium diffusion into the (Al,Sc)N layers and aluminum diffusion into the TiN layers, respectively. On the other hand, scandium appears to diffuse quite rapidly as indicated by a mostly uniform distribution of scandium. Activation energy data for metal diffusion in nitrides is limited [15], but our EDX results indicate that scandium has a higher tendency for diffusion in the TiN/(Al,Sc)N superlattice than titanium and aluminum. The superlattice annealed for 120 hours at 950 °C shows a uniform distribution of all three elements (Ti, Sc, and Al), indicating that a significant amount of intermixing has occurred. It is also worthwhile to note that the aluminum concentration visualized in Figure 2e is decreasing with increased annealing time, a trend that was confirmed by EDX analysis. The loss of aluminum is likely due to surface evaporation after

aluminum is released from the nitride lattice and diffuses to the surface. Released aluminum could also diffuse to the MgO substrate and react with the MgO to form a spinel structure, but our analysis indicates that there is no spinel formation.

Both Setoyama et al. [16] and Kim et al. [17] report that TiN/AlN superlattices exhibit good thermal stability, but their annealing treatments were limited to less than 3.5 hours at 1000 °C. Our 4 hour annealing results agree with both of these reports whereas our extended annealing treatments show significant interdiffusion. Intermixing of nitride superlattices at elevated temperature has also been observed in TiN/CrN [18], TiAlN/CrN [19], TiN/NbN [15], and ZrN/ScN [20] multilayer systems.

Figure 3 shows cross-sectional HRTEM micrographs of the as-deposited and 120 hour/950 °C annealed superlattices. The as-deposited superlattice (Figure 3a) shows distinct layers with coherent interfaces and the Fourier Transform (FT) verifies a cubic crystal structure (inset image). The d-spacing of the first diffraction spots (i.e. 2.11 Å) in the FT corresponds to the cubic phase of (Al,Sc)N where $d_{200}(c\text{-AlN}) = 2.02 \text{ \AA}$ and $d_{200}(c\text{-ScN}) = 2.22 \text{ \AA}$. On the other hand, the superlattice layers are no longer visible after annealing for 120 hours at 950 °C (Figure 3b) and the FT verifies the presence of both cubic and hexagonal grains (inset image) due to the original cubic- $\text{Al}_{0.72}\text{Sc}_{0.28}\text{N}$ phase losing aluminum (cubic- $\text{Al}_{0.72-x}\text{Sc}_{0.28}\text{N}$) and forming the hexagonal-AlN phase. Due to layer interdiffusion the h-AlN grains are distributed randomly throughout the film instead of being concentrated at the original location of the (Al,Sc)N layers. The d-spacing of the 002 cubic-(Al,Sc)N reflection increased due to loss of aluminum.

The HRTEM micrograph (Figure 4a) shows the presence of a cubic matrix with two h-AlN grains of different variants. The cubic and hexagonal crystal structures are confirmed in Figure 4c, which is the FT of Figure 4a, and the diffraction spots are visually highlighted in Figure 4d. As expected, the orientational relationship of the h-AlN diffraction spots with

respect to the cubic lattice observed in the FT are identical to the orientation relationship observed in the 2D x-ray diffraction pattern of Figure 1d. The locations of the h-AlN grains are clearly identified in Figure 4b, which is an inverse FT of Figure 4a while masking the cubic diffraction spots. The inverse FT shows the location of the contrast motif contributing to the hexagonal spot pattern.

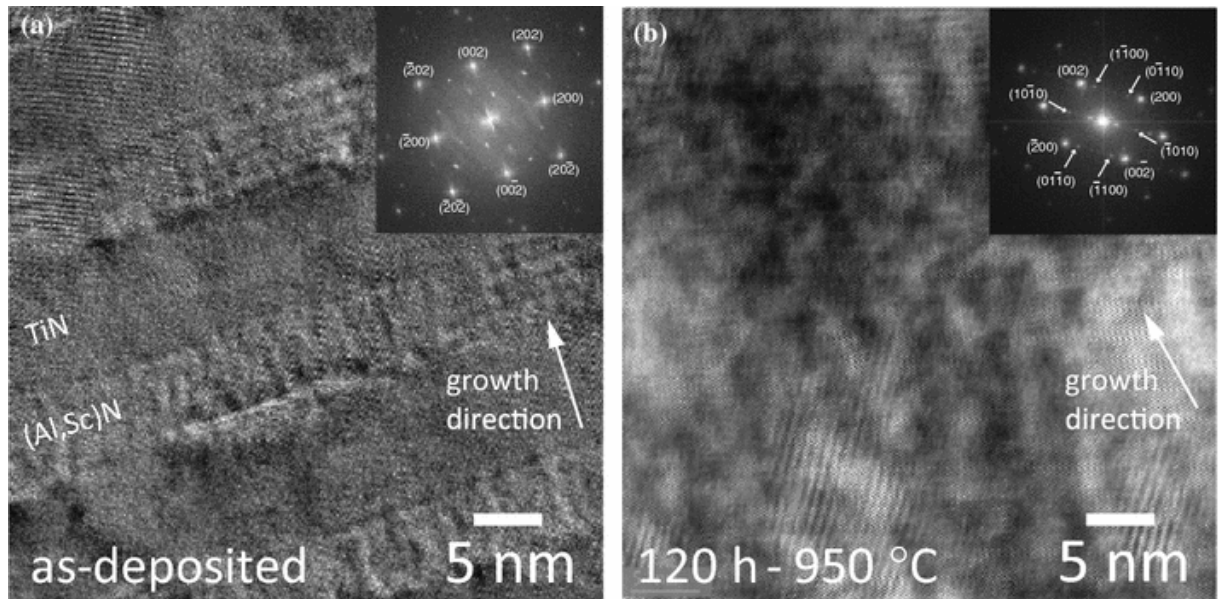


Fig. 3
 HRTEM micrograph of a as-deposited superlattice shows distinct layers with coherent interfaces (inset Fourier Transform (FT) shows cubic structure); b 120 h/950 °C annealed superlattice shows significant intermixing and Moiré fringes (inset FT indicates the presence of cubic and hexagonal grains)

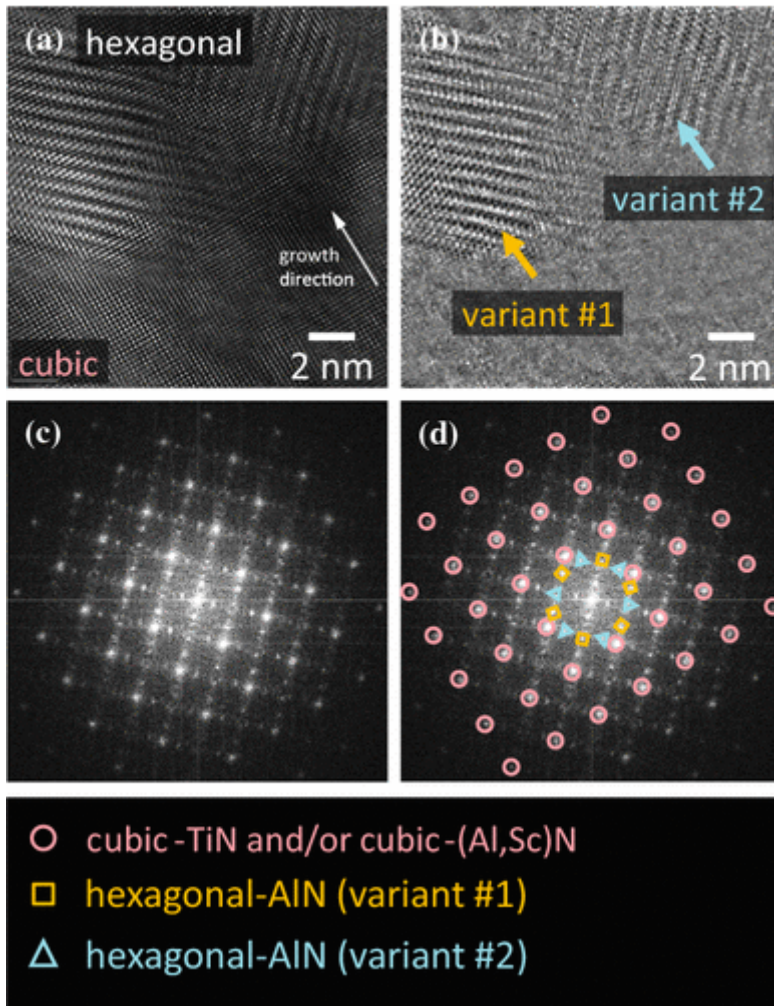


Fig. 4 (color online) a HRTEM micrograph of a superlattice annealed for 120 h at 950 °C. Hexagonal-AlN grains are present within a c-TiN and Al-deficient (Al,Sc)N matrix. b Inverse Fourier Transform of a while masking the cubic diffraction spots shows the location of hexagonal grains. c Fourier Transform of a shows diffraction from the cubic matrix and the two epitaxial variants of h-AlN. d, c overlaid with identification markers (legend at bottom). The Moiré patterns contribute to the intensity found in between the main lattice reflections

Conclusion

TiN/Al_{0.72}Sc_{0.28}N superlattices exhibit limited thermal stability at 950 °C due to interdiffusion and the phase transformation of c-(Al,Sc)N. The superlattice structure is maintained after a 4 hour annealing treatment at 950 °C, but severe interdiffusion of the superlattice layers and the c-Al_{0.72}Sc_{0.28}N → c-Al_{0.72-x}Sc_{0.28}N + h-AlN phase transformation occurs after a 24 hour annealing treatment at 950 °C. The h-AlN grains are randomly

distributed throughout the film due to layer interdiffusion. The application space and maximum operating temperature for TiN/(Al,Sc)N superlattices are thus limited by the kinetics of interdiffusion and the phase transformation. TiN/(Al,Sc)N superlattices may be a viable material for high-temperature applications with short lifetimes (minutes/hours), such as hard coatings in cutting tools, but applications with long lifetimes (months/years), such as thermoelectrics, will require reduced operating temperatures to avoid interdiffusion and phase transformation.

Acknowledgements

JLS and JB acknowledge financial support from Linköping University and the Swedish Research Council (the RÅC Frame Program (2011-6505) and the Linnaeus Grant (LiLi-NFM)). BS and TDS acknowledge financial support by the National Science Foundation and US Department of Energy (CBET-1048616). The Knut and Alice Wallenberg (KAW) Foundation is acknowledged for the Electron Microscope Laboratory in Linköping. Special thanks to Lina Rogström, Niklas Norrby, and Daniel Ostach for assistance with the synchrotron-radiation measurements.

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Figure Captions

Fig. 1 a) as-deposited superlattice is (002)-oriented and displays superlattice reflections and interference fringes in the SAXS signal; b) superlattice reflections are still present after annealing for 4 hours at both 950 °C and 1050 °C; c) superlattice reflections have disappeared and $c\text{-Al}_{0.72}\text{Sc}_{0.28}\text{N}$ has begun to transform into $c\text{-Al}_{0.72-x}\text{Sc}_{0.28}\text{N}$ and h-AlN phases as indicated by 12 diffraction spots from two variants of h-AlN; d) increased annealing time leads to an increased concentration of h-AlN as indicated by darker h-AlN spots; e) schematic of synchrotron-radiation based 2D x-ray diffraction imaging of thin films in transmission mode; f) schematic of two epitaxial variants (offset by 30°) of h-AlN on c-TiN

Fig. 2 (color online) Layer intermixing and loss of superlattice structure with increased annealing time confirmed with a,b) HAADF-STEM micrographs; c,d,e) EDX maps of titanium (Ti), scandium (Sc), and aluminum (Al); f) combined elemental EDX maps

Fig. 3 HRTEM micrograph of a) as-deposited superlattice shows distinct layers with coherent interfaces (inset Fourier Transform (FT) shows cubic structure); b) 120 hr/950 °C annealed superlattice shows significant intermixing and Moiré fringes (inset FT indicates presence of cubic and hexagonal grains)

Fig. 4 (color online) a) HRTEM micrograph of a superlattice annealed for 120 hours at 950 °C. Hexagonal AlN grains are present within a c-TiN and c-Al_{0.72-x}Sc_{0.28}N matrix. b) Inverse Fourier Transform of Fig. 4a while masking the cubic diffraction spots shows the location of hexagonal grains. c) Fourier Transform of Fig. 4a shows diffraction from the cubic matrix and the two epitaxial variants of h-AlN. d) Figure 4c overlaid with identification markers (legend at bottom). The Moiré patterns contribute to the intensity found in between the main lattice reflections