Selectable phase formation in VAIN thin films by controlling Al$^+$ subplantation depth

G. Greczynski$^1,2$, S. Mráz$^3$, L. Hultman$^1$ & J. M. Schneider$^2$

We report on a thin film synthesis technique which allows for unprecedented control over the crystalline phase formation in metastable transition metal nitride based layers. For the model material system $\text{V}_{0.26}\text{Al}_{0.74}\text{N}$, a complete transition from hexagonal to supersaturated cubic structure is achieved by tuning the incident energy, hence subplantation depth, of Al$^+$ metal ions during reactive hybrid high power impulse magnetron sputtering of Al target and direct current magnetron sputtering of V target in Ar/N$_2$ gas mixture. These findings enable the phase selective synthesis of novel metastable materials that combine excellent mechanical properties, thermal stability, and oxidation resistance.

Controlled phase formation of transition metal (TM) nitride based coatings deposited by magnetron sputtering, with numerous applications from wear-resistant coatings on cutting tools and components in automotive engines, is critical as it directly affects the performance. For example, precipitation of thermodynamically-favored wurtzite-AIN (w-AIN) phase in TiAlN-based coatings is well-known to deteriorate mechanical properties$^{1,2}$, while NaCl-cubic structure spinodal decomposition leads to beneficial hardening$^1$. The former presents a great challenge in the design of next generations of TM(N)-based coatings with improved thermal and chemical stability, where alloying with Al to obtain ternary single phase NaCl-structure films is a commonly adopted strategy. Growth of TMAI(N) by conventional DC magnetron sputtering, with low-energy inert-gas ion irradiation of the film surface, typically results in moderate solubility levels, which for the well-studied Ti$_{1-x}$Al$_x$N material system are typically $x_{\text{max}} \sim 0.50$ at growth temperatures $T_\text{g} = 500^\circ \text{C}$.$^3$

Recently, we used VAIN as a model system to illustrate a new concept for the synthesis of metastable single-phase NaCl-structure thin films with Al content far beyond solubility limits obtained with conventional plasma processes. By employing high-intensity temporal fluxes of Al$^+$ metal ions available from high-power pulsed magnetron sputtering (HIPIMS)$^2$ source superimposed onto a continuous V neutral flux supplied from a DC-operated target (hybrid Al-HIPIMS/V-DCMS co-sputtering)$^6$–$^8$ we demonstrated single-phase NaCl-structure $\text{V}_{1-x}\text{Al}_x\text{N}$ films ($c$-VAIN) with an unprecedented metastable Al solubility limit of $x_{\text{max}} = 0.75^{9,10}$, significantly higher than $x_{\text{max}} = 0.52$ obtained with DCMS$^{9,12}$. This was achieved by separating film-forming species in time and energy domains by applying high-amplitude (300 V) low duty cycle (5%) negative substrate bias synchronized with the Al-rich portion of the HIPIMS pulse. The V atoms, predominantly deposited between HIPIMS pulses, reside at the very surface where high adatom mobility and gas-ion-induced mixing drives the system towards thermodynamic equilibrium to form high-VN-content $c$-VAIN crystallites. In contrast, $\sim 300$ eV Al$^+$ ions, arriving at the film exclusively during the $\sim 100$-μs-long metal-ion rich HIPIMS phase, are directly implanted into $c$-VAIN grains buried below the surface, the process we called subplantation. As the activation energy for bulk diffusion is larger than for surface diffusion, the mobility on the cation lattice is limited enabling the formation of metastable, supersaturated NaCl-VAIN solid solutions. This scenario is in distinct contrast to conventional DC magnetron sputtering, with no time- or energy-separation of sputtered species, in which both V and Al are co-deposited as neutrals, hence coexist at the surface where adatom diffusion is high, resulting in precipitation of the thermodynamically stable w-AIN phase as the Al concentration exceeds that of V.

Here, we present direct experimental evidence that the Al subplantation technique allows for a full control over phase formation in VAIN layers. For the $\text{V}_{1-x}\text{Al}_x\text{N}$ with $x = 0.74$, a complete transition from single-phase wurtzite to supersaturated single-phase NaCl structure is achieved by increasing the implantation depth of Al$^+$ metal-ions, which scales with the incident Al$^+$ ion energy. The latter is controlled by varying the amplitude of the

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$^1$Thin Film Physics Division, Department of Physics (IFM), Linköping University, SE-581 83, Linköping, Sweden.
$^2$Materials Chemistry, RWTH Aachen University, Köpenikusstr. 10, D-52074, Aachen, Germany. Correspondence and requests for materials should be addressed to G.G. (email: grzgr@ifm.liu.se)
substrate bias pulse synchronized with the metal-ion-rich portion of HIPIMS flux, using the input from the in situ time-resolved ion mass spectrometry measurements performed at the substrate position.

Methods

$V_{1-x}Al_xN$ films are grown on $1.5 \times 2 \text{ cm}^2 \text{ Si(001)}$ substrates in an industrial CemeCon AG CC800/9 magnetron sputtering system,13 equipped with Advanced Energy Pinnacle Plus and Melec SIPP2000USB-10-500-S pulser combined with 10 kW ADL GX 100/1000 DC power supply, using V and Al targets assembled from two triangular pieces that form rectangular plates with dimensions $8.8 \times 50 \text{ cm}^2$. Substrates are mounted symmetrically with respect to the targets on a $12 \times 31 \text{ cm}^2$ metal plate arranged in a co-sputtering geometry such that the angle between the substrate normal and the target normal is $\sim 28^\circ$, and the target-to-substrate distance is 18 cm (see Fig. 1). The system base pressure is lower than 0.75 mPa ($5.63 \times 10^{-6} \text{ Torr}$), following the 1 h $40 \pm 5 \text{ min}$–long heating step, and the total pressure during deposition is 0.42 Pa (3 mTorr) with a nitrogen flow fraction in the sputtering gas, $N_2/(N_2+Ar)$, varied from 0.29 to 0.32. Substrate temperature $T_s$ during deposition is $\sim 500 \degree C$. The vacuum chamber is vented at a substrate temperature lower than 180 °C to allow for a better control of surface chemistry upon air exposure.

The Al target operates in HIPIMS mode, while the V target is powered by a DC generator (Al-HIPIMS/V-DCMS). The average HIPIMS power is fixed at 2.5 kW (pulsing frequency $f = 500 \text{ Hz}$, pulse time $\tau_{\text{HIP}} = 50 \mu \text{s}$), while the power to the DC magnetron is varied from 1.20 to 0.54 kW resulting in $V_{1-x}Al_xN$ compositions ranging from $x = 0.53$ to 0.80, and the total film thickness between 1490 and 1050 nm. The film growth rates are in the range $16.6$ to $11.7 \text{ nm/min}$, or $5.5 \times 10^{-4}$ to $3.9 \times 10^{-4} \text{ nm per period (1/f)}$, thus several hundred HIPIMS pulses are necessary to grow one monolayer. A negative pulsed substrate bias $V_s$ ranging from floating (on average $-15 \text{ V}$) to $-400 \text{ V}$, synchronized to each HIPIMS pulse, is used. The bias pulse time $\tau_s$ and an offset $\tau_{\text{offset}}$ are kept constant at 100 and $30 \mu \text{s}$, respectively, hence, the resulting bias duty cycle is 5%. Between HIPIMS pulses, the substrate is at floating potential, $V_f = -10 \text{ V}$, due to the DC magnetron (with V target) that operates continuously. The floating potential is measured with digital oscilloscope. In addition, $V_{0.26}Al_{0.74}N$ films are grown with $V_s = -300 \text{ V}$ using (a) $\tau_{\text{offset}} = 50 \mu \text{s}$ and $\tau_s = 30 \mu \text{s}$, and (b) $\tau_{\text{offset}} = 30 \mu \text{s}$ and $\tau_s = 130 \mu \text{s}$.

Compositions of $V_{1-x}Al_xN$ films are determined by energy-dispersive x-ray spectroscopy (EDX) performed with EDAX instrument attached to JEOL scanning electron microscope JSM-6480 using ToF-ERDA analyzed samples as a standard. Philips X’Pert MRD system operated with point-focus Cu Kα radiation ($\lambda = 1.5418 \text{ Å}$) is used for x-ray diffraction (XRD) scans and residual stress analyses by sin²ψ technique. The latter is conducted by means of $0-2\theta$ scans obtained as a function of the sample tilt angle ψ defined as the angle between surface normal and the diffraction plane containing the incoming and diffracted x-ray beams. ψ is varied from 0 to

![Figure 1. The schematic overview of the deposition setup. Only two cathodes indicated at the bottom are used in the present experiments. All depositions are performed in a stationary configuration.](image-url)
fractions the underlying physical mechanisms can be gained from the comparison of Fig. 4, where the relative volume \( \psi \) are single phase, with the NaCl structure. The 111 and 002 diffraction peaks recorded at the strain-free angle to the severe gas rarefaction caused by very high temporal fluxes originating from the HIPIMS source 18–20. Based on the time evolution of Al\( ^+ \) flux with respect to that of gas ions, the offset and duration of the bias pulse can be selected in order to precisely synchronize \( V_s(t) \) to the Al\( ^+ \)-rich portion of each HIPIMS pulse and, hence, insure Al\( ^+ \) subplantation.

Figure 3 shows the most representative sets of \( \theta-2\theta \) XRD scans obtained as a function of the sample tilt angle \( \psi \) defined as the angle between surface normal and the diffraction plane containing the incoming and diffracted x-ray beams, for \( V_{0.26}Al_{0.74}N \) films grown with (a) \( V_s = -60 \) V, and (b) \( V_s = -300 \) V. In both cases, bias pulses are synchronized to the metal-ion rich portion of the HIPIMS discharge, implying the offset of 30 ms and the pulse duration of 100 \( \mu \)s. The only diffraction peaks in the former case are those from w-AlN, indicative of a w-AlN phase, estimated from wurtzite \( \alpha \)-AlN to 3.160 Å and 5.073 Å, respectively. Based on the time evolution of Al\( ^+ \) ion flux with respect to that of gas ions, the offset and duration of the bias pulse can be selected in order to precisely synchronize \( V_s(t) \) to the Al\( ^+ \)-rich portion of each HIPIMS pulse and, hence, insure Al\( ^+ \) subplantation.

In distinct contrast, \( V_{0.26}Al_{0.74}N \) films grown under identical conditions but with \( V_s = -300 \) V (Fig. 3(b)) are single phase, with the NaCl structure. The 111 and 002 diffraction peaks recorded at the strain-free angle \( \psi^\circ \) are shifted towards higher diffraction angles with respect to the reference VN powder patterns (e.g. 2\( \theta_{111} = 37.86^\circ \) vs. 37.61\(^\circ \) for powder sample) due to incorporation of smaller Al atoms into the cubic lattice. The lattice shrinkage is, however, relatively small as compared to the well-studied TiAlN system, due to significantly lower lattice constant of VN (4.139 Å) with respect to that of TiN (4.242 Å). The relaxed lattice parameter \( a_0 \) extracted from the 111 and 002 peak positions recorded at \( \psi = \psi^\circ \) is 4.113 Å. Both 111 and 002 XRD reflections exhibit a shift to higher 2\( \theta \) angles with increasing \( \psi \), indicative of lattice expansion caused by incorporation of larger V atoms. The relaxed lattice constants increase from \( a_0 = 3.111 \) Å and \( c_0 = 4.979 \) Å for w-AlN to 3.160 Å and 5.073 Å, respectively.

Thus, by varying the amplitude of the synchronous low-duty-cycle bias pulse, while maintaining all other parameters constant, the phase content of \( V_{0.26}Al_{0.74}N \) films can be altered completely from thermodynamically-preferred wurtzite with \( V_s = -60 \) V to metastable NaCl-structure obtained with \( V_s = -300 \) V. More insight into the underlying physical mechanisms can be gained from the comparison of Fig. 4, where the relative volume fractions \( \chi \) of w-AlN phase, estimated from wurtzite 10\( \bar{1} \)0 and NaCl 002 peak intensities integrated over all \( \psi \)
angles, are plotted as a function of synchronous bias voltage $V_s$. Clearly, with increasing $V_s$, the relative $w$-AlN content decreases rapidly from $\chi = 1$ with $V_s = -60$ V to 0.91, 0.39, 0.19, and 0.03 for bias amplitude gradually increasing to $-100$, $-130$, $-165$, and $-200$ V. For $|V_s| \geq 250$ V, the $w$-AlN fraction is below detection limits. The single phase NaCl structure obtained with higher $V_s$ has been confirmed with selected area electron diffraction in Figure 3.

Figure 3. XRD $\theta$–$2\theta$ scans as a function of the tilt angle $\psi$ for $V_{0.26}A_{0.74}N$ films grown with the synchronous bias voltage of (a) $-60$ V, and (b) $-300$ V. “S” denotes the forbidden 002 reflection from the Si substrate, which appears due to multiple scattering.

Figure 4. 1010 $w$-AlN and 002 NaCl $c$-VN peak area ratios obtained from $V_{0.26}A_{0.74}N$ films, integrated over all $\psi$ angles, and normalized to random powder XRD patterns plotted as a function of the synchronous bias voltage. The insert shows Al$^+$ implantation profiles obtained from TRIDYN simulations as a function of Al$^+$ energy.
Figure 5. A phase content map for V$_{1-x}$Al$_x$N films with 0.53 $\leq x \leq$ 0.80, grown with the synchronous negative bias voltage with the amplitude in the range (floating) 15 $\leq |V_s| \leq$ 400 V. The green dashed curve serves as an eye-guide to the regions of single-phase cubic films (solid red squares) and two-phase layers (open blue triangles) containing both cubic and w-AlN grains.

(Figure 5)
As long as V flux dominates over that of Al, formation of high V content metastable, cubic VAlN prevails on the surface. Once the Al flux dominates over that of V, the driving force for the formation of thermodynamically stable \( w \)-AlN phase increases and, eventually, nucleation of the wurtzite phase takes place. With \( V_s = -20 \) V this is observed for \( x = 0.58 \) (see Fig. 5).

With increasing the amplitude of negative substrate bias, the implantation depth for the ionized portion of the Al flux increases and eventually, at \(-eV_s \geq 200\) eV, the majority of Al\(^+\) is subplanted below the high-mobility zone. The composition at the surface is set by the V atoms deposited predominantly between HIPIMS pulses and the non-ionized portion of the Al-HIPIMS flux, both arriving with an energy of a few eV. Since a significant portion of the Al flux during Al-HIPIMS is ionized, the Al concentration at the surface is lowered (for constant settings on the Al-HIPIMS source) due to subplantation, preventing the formation of the hexagonal phase (which is otherwise observed) in the high-mobility surface zone. Al\(^+\) is subplanted directly into the cubic V-rich V\(_{1-x}\)Al\(_x\)N matrix triggering local mobility on cation lattice and subsequent quenching, thus enabling the formation of cubic metastable solid solutions. As the activation energy for bulk diffusion is larger than for surface diffusion, the mobility on the cation lattice is limited to few neighboring sites. It appears that the subplantation induced mobility is insufficient to cause nucleation and growth of hexagonal AlN with a larger molar volume than the resulting Al supersaturated c-VAIN phase. Eventually, in the limit of \(|V_s| \gtrsim 250\) V, the vast majority of Al\(^+\) is subplanted below the surface, and \( x_{\text{max}}(V_s) \) is limited by the ionization degree of the Al-HIPIMS flux. The latter is reflected in the \( x_{\text{max}}(V_s) \) plot in Fig. 5 which shows a clear saturation at higher \( V_s \) values.

Figure 6 presents direct experimental evidence for the critical influence of the bias pulse synchronization (pulse offset and pulse duration) with the Al\(^+\) portion of the HIPIMS pulse on the phase formation. Two sets of \( \theta-2\theta \) XRD scans recorded as a function of the sample tilt angle \( \psi \) are shown for V\(_{0.26}\)Al\(_{0.74}\)N films grown with \( V_s = -300\) V and (a) 30-\(\mu\)s-long pulses with a 50-\(\mu\)s offset, and (b) 130-\(\mu\)s-long pulses with a 30-\(\mu\)s offset. "S" denotes the forbidden 002 reflection from the Si substrate, which appears due to multiple scattering.
130 μs starting from 30 μs after ignition of the HIPIMS discharge. In contrast to the single-phase NaCl-structure V_{0.28}Al_{0.72}N film obtained with 30 μs offset and 100-μs-long bias pulses (see Fig. 3(b)), both layers are two-phase with clear contributions of w-AlN. In addition, NaCl-structure diffraction signals exhibit reduced intensity and are broader. In the case of too short bias pulses (Fig. 6(a)), a fraction of the Al^3+ flux is not subplanted, and is, hence, deposited onto the very surface where high mobility removes kinetic constraints, resulting in precipitation of w-AlN. For too long pulses (Fig. 6(b)), a second phase appears as a consequence of high-energy Ar^+ (N_2^+) bombardment, which induces point defects that may serve as nucleation sites for the formation of w-AlN precipitates at relatively low AlN concentrations.

The here presented experimental evidence clearly illustrates that coating synthesis strategies based on separating ion bombardment of the film forming metallic species in time and energy domains allows for unprecedented enhancements in metastable Al solid solubility in transition metal alumina nitrides with low or moderate compressive stress levels, varying from −1.6 GPa with x = 0.53 to −3.8 GPa for x = 0.74. Hardness and elastic moduli of Al-HIPIMS/V-DCMS V_{1-x}Al_{x}N films with x between 0.68 and 0.74 remain high, at respectively ~30 and ~325 GPa. The H/E(x) ratio reflecting the materials resistance against plastic deformation and considered to be an important design criterion is 0.25–0.30.

Furthermore, a substantial improvement of high temperature oxidation resistance can be expected (based on the significantly enhanced critical Al solubility) which is a significant advantage over conventional processing methods.

Conclusions

In summary, we present a novel thin film synthesis method, which allows for a complete control over the phase formation in metastable transition metal nitride layers. The technique is based on hybrid high power impulse and magnetron co-sputtering of elemental targets in Ar/N_2 gas mixture with precise synchronization of the substrate bias pulse to the Al^3+-populated portion of the HIPIMS discharge. For the model material system of V_{1-x}Al_{x}N with a high Al content on the cation lattice x = 0.74, a complete transition from hexagonal w-AlN to supersaturated cubic NaCl structure is achieved by increasing the Al^3+ energy, ceteris paribus, by subsequently increasing the subplantation depth of Al^3+ ions, as indicated by Monte Carlo TRIDYN simulations. The former is easily controlled by varying the amplitude of the synchronous low-duty-cycle substrate bias pulse.

Data Availability. The data and samples analyzed during the current study are available from the corresponding author on reasonable request.

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Author Contributions
G.G. and S.M. planned the study and conducted film growth. S.M. performed ion mass spectrometry measurements. G.G. conducted the analysis and prepared the first draft of the manuscript. L.H. and J.M.S. took part in the planning of the study, provided data interpretation and discussion, and were engaged in the writing of the manuscript.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

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