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Extended metastable Al solubility in cubic VAlN by metal-ion bombardment during pulsed magnetron sputtering: film stress vs subplantation

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Abstract

Dynamic ion-recoil mixing of near-film-surface atomic layers is commonly used to increase the metastable solubility limit x_{max} in otherwise immiscible thin film systems during physical vapor deposition. Recently, Al subplantation achieved by irradiating film growth surface with Al^+ metal-ion flux was shown to result in an unprecedented x_{max} for VAlN, far above values obtained with gas ion irradiation. However, it is reasonable to assume that ion irradiation necessary for subplantation also leads to a compressive stress σ buildup. In order to separate the effects of Al^+ bombardment on σ and x_{max} , and realize low-stress high- x_{max} nitride alloys, we grow metastable cubic $\text{V}_{1-x}\text{Al}_x\text{N}$ ($0.17 \leq x \leq 0.74$) films using reactive magnetron sputtering under different ion irradiation conditions. Al and V targets are operated in Ar/ N_2 discharges employing (i) conventional DC (Ar^+ , N_2^+), (ii) hybrid HIPIMS/DC processing with one type of metal ions present (Al^+ or V^+/V^{2+}), and (iii) HIPIMS with concurrent Al^+ and V^+/V^{2+} fluxes. Comparison to *ab initio* calculated Al solubility limit reveals that $x_{max} = 0.55$ achieved with V^+/V^{2+} irradiation is entirely accountable for by stress. In contrast, Al^+ fluxes provide a substantial increase in x_{max} to 0.63, which is 12% higher than expected based on the stress-induced increase in metastable solubility. Correlative stress and atom probe tomography data confirm that the metastable Al

solubility enhancement is enabled by Al^+ subplantation. The here proposed processing strategy allows for growth of single-phase cubic nitride alloys with significantly increased Al concentrations embodying tremendous promise for substantial improvements in high temperature oxidation resistance and mitigates the risk of stress-induced adhesive or cohesive coating failure.

1. Introduction

Alloying with Al is a common design strategy for increasing thermal stability and oxidation resistance of transition metal (TM) nitride based thin films with wide range of applications, such as wear-protective coatings on cutting tools and components in automotive engines. As the metastable solubility of Al in NaCl-structure TMN's is limited, the great challenge lies in increasing Al concentration while avoiding precipitation of the softer wurtzite AlN phase (*w*-AlN). Low-energy inert-gas ion irradiation of the film surface during TMN growth by conventional DC magnetron sputtering typically results in moderate solubility levels, which for the well-studied $\text{Ti}_{1-x}\text{Al}_x\text{N}$ materials system are typically $x_{\max} \sim 0.50$ at growth temperatures $T_s = 500$ °C.^{1,2} Significantly higher $x_{\max}$ values up to 0.67 have been reported using cathodic arc evaporation, where the growing film surface is subject to intense fluxes of ionized film-forming species.^{3,4} Based on *ab initio* data communicated by Mayrhofer et al.⁵ this can at least in part be rationalized by considering the Al distribution on the metal sublattice, which is affected by the deposition conditions.

Intense ion bombardment is often associated with an increase in compressive stress σ , values up to -9.1 GPa have been reported,⁶ and typically scale with the magnitude of the applied substrate bias potential.^{7,8,9,10,11} It is well known that compressive stresses influence the phase stability in ternary TMN's and act to increase the metastable solubility.^{12,13,14,15,16} For TiAlN and CrAlN systems, the *ab initio* calculations of Holec et al.¹³ thus indicated an increase in $x_{\max}$ by 0.1 for $\sigma = -4$ GPa.

High-power pulsed magnetron sputtering (HIPIMS)¹⁷ provides an alternative route for ion-assisted TM nitride film growth by employing a substrate bias potential that is synchronized with the HIPIMS pulse and, hence, with the metal-ion-rich fraction of the deposition flux.^{18,19} It was

shown for $\text{Ti}_{1-x}\text{Al}_x\text{N}$ and $\text{Ti}_{1-x}\text{Si}_x\text{N}$ films deposited in a hybrid high-power pulsed and DC magnetron (HIPIMS/DC) co-sputtering configuration that film nanostructure, phase composition, and stress evolution exhibit distinct differences depending upon which metal target was powered by HIPIMS.^{20,21,22} The effects were ascribed to differences in mass and charge state of metal-ions incident on the growing film surface,²³ and the detrimental role of intense fluxes of doubly-ionized Ti atoms, resulting from the fact that the second ionization potential IP_{Ti}^2 of Ti is lower than the first ionization potentials of Ar and N_2 .

Recently, we demonstrated single-cubic-phase $\text{V}_{1-x}\text{Al}_x\text{N}$ films (*c*-VAlN) with an unprecedented metastable Al solubility limit of $x_{max} = 0.75$, which is 42 % higher than $x_{max} = 0.52$ obtained with conventional magnetron sputtering techniques.²⁴ This increase was achieved by employing high-intensity temporal fluxes of Al^+ metal ions from pulsed HIPIMS source superimposed onto a continuous V neutral flux supplied from a DC-operated target (hybrid Al-HIPIMS/V-DC co-sputtering) which allowed for separation of the film forming species in time and energy domains. The application of high-amplitude (-300 V) substrate bias synchronized with the Al-rich portion of the HIPIMS flux (70-100 μs into the pulse) enables incorporation of energetic Al^+ ions directly into *c*-VAlN grains buried below the surface, which we refer to as *subplantation*. That, together with a simultaneous supply of N^+ present during the metal phase of the HIPIMS pulse,²⁵ generated local mobility on the cation lattice to form a supersaturated *c*-VAlN solid solution. This film growth scenario differs essentially from the conventional DC magnetron sputtering, in which both Al and V coexist at the surface where adatom diffusion and gas-ion-induced mixing prevent the formation of supersaturated *c*-VAlN and the precipitation of *w*-AlN is observed when the Al concentration exceeds that of V.

Since metal-ion subplantation, as any other form of ion bombardment, typically affects the

film stress state, the question arises whether the unprecedented increase in x_{max} observed upon Al^+ irradiation is due to the stress-induced stabilization. To address this issue we designed a series of experiments employing $\text{V}_{1-x}\text{Al}_x\text{N}$ system ($0.17 \leq x \leq 0.74$), where the ion irradiation conditions are varied during film growth, from gas ion bombardment (Al/V-DC), through one type of metal ion flux at the time, Al^+ vs. V^+/V^{2+} , (Al-HIPIMS/V-DC vs. V-HIPIMS/Al-DC), to the concurrent metal ion bombardment by Al^+ and V^+/V^{2+} (Al-HIPIMS/V-HIPIMS). Correlative analysis of the experimentally obtained x_{max} and σ values with *ab initio* calculations allows to unravel the relative contributions of stress and subplantation for the Al supersaturation in $\text{V}_{1-x}\text{Al}_x\text{N}$ system ($0.17 \leq x \leq 0.74$).

2. Experimental

2.1. Film growth

$\text{V}_{1-x}\text{Al}_x\text{N}$ films are grown on $1.5 \times 2 \text{ cm}^2$ Si(001) substrates in an industrial CemeCon AG CC800/9 magnetron sputtering system,²⁶ equipped with Melec SIPP2000USB-10-500-S pulser and 10 kW ADL GX 100/1000 DC power supplies, 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 the $12 \times 31 \text{ cm}^2$ 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. The system base pressure is lower than 0.75 mPa (5.63×10^{-6} Torr), following the 1 h 40 ± 5 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, $\text{N}_2/(\text{N}_2 + \text{Ar})$, varied from 0.29 to 0.32. Substrate temperature T_s during deposition is $\sim 500^\circ\text{C}$. The vacuum chamber is vented at

the substrate temperature lower than 180 °C to allow for a better control of surface chemistry upon air exposure.²⁷

Four different powering schemes are employed to deposit four series of $V_{1-x}Al_xN$ films with varying Al/(Al+V) ratio x , with distinctly different ion irradiation conditions during growth. Two first series are obtained using a hybrid process in which one of the targets is operated in HIPIMS mode, while the other runs as a conventional magnetron (Al-HIPIMS/V-DC and V-HIPIMS/Al-DC). For each series, the average HIPIMS power P_{HIPIMS} , frequency f , and cathode pulse length τ_{HIPIMS} , are maintained constant, while power to the DC magnetron P_{DC} is varied to control film compositions. In the Al-HIPIMS/V-DC configuration, $P_{Al-HIPIMS} = 2.5$ kW ($f = 500$ Hz, $\tau_{HIPIMS} = 50$ μ s), while P_{V-DC} is varied from 4 to 0.8 kW resulting in $V_{1-x}Al_xN$ compositions ranging from $x = 0.23$ to 0.72, film growth rates varying from 37.7 to 15.5 nm/min, and the film thickness between 2260 and 1660 nm (obtained by adjusting the deposition time in the range 60 to 120 min). For experiments carried out in the V-HIPIMS/Al-DC mode, $P_{V-HIPIMS} = 3.35$ kW ($f = 500$ Hz, $\tau_{HIPIMS} = 50$ μ s) with P_{Al-DC} varied from 0.83 to 4.15 kW providing films with $x = 0.23$ to 0.74. The film growth rates range from 13.6 to 44.1 nm/min, while the film thickness varies between 1650 and 1800 nm (as a result of adjusting the deposition time from 73 to 135 min). Higher $P_{V-HIPIMS}$ was necessary in order to maintain peak target current $I_{V-HIPIMS}^{max}$ on the similar level, ~ 400 A, as $I_{Al-HIPIMS}^{max}$ during Al-HIPIMS/V-DC.

In the third powering scheme investigated, both targets are operated in HIPIMS mode (Al-HIPIMS/V-HIPIMS) with $\tau_{HIPIMS} = 50$ μ s. The $V_{1-x}Al_xN$ film compositions are tuned by varying the relative number of Al-HIPIMS vs. V-HIPIMS pulses within the synchronized pulse packages of the length from 2 to 80 ms, while maintaining both $I_{V-HIPIMS}^{max}$ and $I_{Al-HIPIMS}^{max}$ on the similar level, ~ 400 A, as during hybrid film growth. This corresponds to varying $P_{Al-HIPIMS}/P_V$.

HIPIMS power ratio from 0.42 to 2.08 resulting in films with compositions in the range $0.17 \leq x \leq 0.72$, film growth rates varying from 12.7 to 17.4 nm/min, and the film thickness between 1910 and 3220 nm (deposition time adjusted in the range 120 to 202 min).

Finally, in the fourth scheme, a combinatorial approach is used with two identical split Al/V targets operating in DC mode (Al/V-DC) at $P_{Al/V-DC} = 3$ kW. $V_{1-x}Al_xN$ films with composition varying from $x = 0.32$ to 0.71 are obtained in one single process run by placing the substrates at different heights in the chamber with the target-to-substrate distance fixed. The film growth rates range from 28.3 to 55.0 nm/min, while the film thickness is between 1700 and 3300 nm (deposition time of 60 min).

A pulsed substrate bias with the amplitude $V_s = -100$ V and length $\tau_s = 200$ μ s, synchronized to each HIPIMS pulse, is used in Al-HIPIMS/V-DC, V-HIPIMS/Al-DC, and Al-HIPIMS/V-HIPIMS experiments. Hence, the resulting bias duty cycle is 10% for hybrid configurations and 10-20% for purely HIPIMS film growth. Between HIPIMS pulses, the substrate is at floating potential, $V_f = -10$ V. For $V_{1-x}Al_xN$ growth in Al/V-DC configuration a continuous DC bias with $V_s = -100$ V is employed throughout the deposition.

2.2. Film characterization

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. Film thicknesses are obtained from cross-sectional scanning electron microscopy (XSEM) analyses in a LEO 1550 instrument. Philips X'Pert MRD system operated with point-focus Cu $K\alpha$ radiation is used for θ - 2θ x-ray diffraction (XRD) scans and residual stress analyses by $\sin^2\psi$ technique.²⁸ θ - 2θ scans are 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 71.57° , with steps chosen to produce equally-spaced data points on the $\sin^2\psi$ axis. $V_{1-x}Al_xN$ relaxed lattice parameters a_o are determined from θ - 2θ scans acquired at the strain-free tilt angle ψ^* defined as $\psi^* = \arcsin[(2\nu/(1+\nu))^{1/2}]$,²⁸ in which ν is the Poisson ratio. As no $\nu(x)$ values are reported for $V_{1-x}Al_xN$ we use linear extrapolation between 0.27 for VN ($x = 0$) and 0.15 for c-AlN ($x = 1$),²⁹ corresponding to ψ^* varying from ~ 41 to $\sim 31^\circ$. The differential thermal contraction stress correction, which arises during cooling of the samples from T_s to RT, is calculated using the average thermal expansion coefficient of Si(001) $\alpha = 2.9 \times 10^{-6} \text{ K}^{-1}$.³⁰ Since α for $V_{1-x}Al_xN$ films is unknown, we use a linear extrapolation between $\alpha_{VN} = 9.35 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{AlN} = 8.00 \times 10^{-6} \text{ K}^{-1}$ from Ref. 31. Nanoindentation hardness H and elastic modulus E of $V_{1-x}Al_xN$ alloy films are obtained for each sample in UMIS instrument equipped with a Berkovich diamond tip using a minimum of 20 indents, each with a maximum load of 15 mN. Indentation depths are not allowed to exceed 10% of the film thickness in order to minimize substrate effects. Load-displacement curves are analyzed using the method of Oliver and Pharr.³² Samples for cross-sectional TEM (XTEM) analyses are prepared by mechanical polishing, followed by Ar^+ ion milling at 5 kV with an 8° incidence angle and sample rotation. During the final thinning stages, the ion energy and incidence angle are reduced to 2.5 kV and 5° . Film nanostructure is analyzed in a FEI Tecnai G2 TF 20 UT transmission electron microscope operated at 200 kV. Spatially-resolved chemical composition distribution analysis is carried out by 3D atom probe tomography (APT) using a CAMECA LEAP 4000X HR system. Field evaporation is triggered by 30 pJ energy laser pulses at a frequency of 250 kHz and the specimen temperature is kept at 60 K. Needle-like APT specimens are prepared by lift-outs from $V_{1-x}Al_xN$ ($x = 0.45$, and 0.58) thin film cross-sections, hence, the tips are oriented perpendicular to the growth direction.

3. Computational details

Ab initio calculations are carried out using density functional theory (DFT),³³ as implemented in the Vienna Ab Initio Simulation Package (VASP),^{34,35} wherein projector augmented wave potentials³⁶ are employed. The generalized gradient approximation,³⁷ a convergence criterion for relaxation of 0.01 meV and Blöchl corrections for the total energy³⁸ cut-off of 500 eV are applied. Brillouin zone integration is carried out with a $6 \times 6 \times 6$ and $9 \times 9 \times 5$ Monkhorst-Pack k-point mesh³⁹ for cubic and wurtzite $V_{1-x}Al_xN$, respectively. $2 \times 2 \times 2$ supercells with 64 atoms arranged in the C#3 way according to Mayrhofer et al.⁵ are utilized for cubic $V_{1-x}Al_xN$, whereas $2 \times 2 \times 2$ supercells containing 32 atoms are used for ZnS-wurtzite $V_{1-x}Al_xN$, where Al and V atom layers are stacked on the metal sublattice in c-direction. Full structural relaxation is performed for every configuration. Utilizing the Birch-Murnaghan equation of state,⁴⁰ the equilibrium volume data are obtained. The pressure-dependent maximum AlN mole fraction solubility in cubic $V_{1-x}Al_xN$ is estimated from the crossovers of the third-order polynomials fitted enthalpy data (ΔH) of cubic and wurtzite $V_{1-x}Al_xN$ at different hydrostatic pressures according to the method introduced by Holec et al.¹³ The pressure-dependent enthalpy of formation for the cubic and wurtzite solid solutions are obtained from the equilibrium total energy difference between the calculated phases and the respective elements.

4. Results

4.1. Discharge characteristics

The overall shape of $V(t)$ and $I(t)$ functions (shown in Fig. S1 of the supplementary material) is essentially the same for all HIPIMS depositions and characterized by a constant pulse voltage and pulse current increasing linearly with time. The peak target current values I_{HIPIMS}^{max} reached towards the end of the HIPIMS pulse and the average $V(t)$ amplitude during the pulse

$\bar{V}_{HIPIMS}$ depend to some extent on the powering scheme used. $I_{Al-HIPIMS}^{max}$ during Al-HIPIMS/V-DC increases with decreasing P_{V-DC} (corresponding to increasing Al content in the film), from 368 A with $P_{V-DC} = 4$ kW ($x = 0.23$) to 422 A with $P_{V-DC} = 0.8$ kW ($x = 0.72$), while $\bar{V}_{Al-HIPIMS}$ drops from 541 to 492 V. This can be explained by an increasing nitriding of the Al target as P_{V-DC} decreases, which leads to an enhanced electron emission due to secondary electron emission coefficient I_{SEE} of AlN being ~140% higher than that of a metal.⁴¹ In contrast, during V-HIPIMS/Al-DC growth both $I_{V-HIPIMS}^{max}$ and $\bar{V}_{V-HIPIMS}$ are essentially constant at 401 A and 686 V, respectively, presumably due to lower heat of VN formation than that of AlN (-217 vs. -318 kJ/mol), which prevents poisoning of the V target.⁴² Thus, while $\bar{V}_{V-HIPIMS}$ is significantly higher than $\bar{V}_{Al-HIPIMS}$ the peak target current values in both powering schemes are within the same range.

In the Al-HIPIMS/V-HIPIMS configuration, $\bar{V}_{V-HIPIMS}$ values are essentially identical to those measured during V-HIPIMS/Al-DC, while $I_{V-HIPIMS}^{max}$ data points are in the range from 392 to 438 A. In the case of Al target, $I_{Al-HIPIMS}^{max} = 400 \pm 18$ A and $\bar{V}_{Al-HIPIMS} = 483 \pm 31$ V, both on similar level as during Al-HIPIMS/V-DC.

The time-averaged ion/metal flux ratios J_i/J_{Me} measured at the substrate position for all four target configurations employed here are plotted in Fig. S2 of the supplementary material as a function of x . The lowest J_i/J_{Me} is encountered during Al/V-DC film growth, where ion/metal flux ratio decreases from 0.9 with $x = 0.32$ to 0.3 with $x = 0.71$, *i.e.*, values are typical for DCMS discharges.⁴³ Interestingly, in the case of Al-HIPIMS/V-DC J_i/J_{Me} increases from 1.1 with $x = 0.23$ to 2.4 with $x = 0.72$ predominantly due to the decreasing neutral flux from the V target (decreasing P_{V-DC}), at the constant ion flux per pulse (constant $P_{Al-HIPIMS}$). The opposite trend is observed for the V-HIPIMS/Al-DC configuration where the Al-DC flux increases with increasing Al content (increasing P_{Al-DC} at constant $P_{V-HIPIMS}$), resulting in J_i/J_{Me} decreasing from 2.7 with x

= 0.23 to 1.0 with $x = 0.74$. This symmetry in $J_i/J_{Me}(x)$ plots between both hybrid configurations indicates that ion fluxes obtained from Al-HIPIMS and V-HIPIMS sources are indeed comparable, presumably due to the fact that similar peak current densities are used. In the pure HIPIMS configuration, J_i/J_{Me} is roughly a sum of values obtained in respective hybrid processes and varies from 4.8 to 3.4 with x in the range 0.17-0.72.

4.2. $V_{1-x}Al_xN$ Film growth

Fig. S3 of the supplementary material shows a plot of Al concentration relative to x for three sets of $V_{1-x}Al_xN$ films grown with different target configurations as a function of Al-to-V power ratio P_{Al}/P_V . Clearly, for any P_{Al}/P_V value, highest x is obtained with V-HIPIMS/Al-DC configuration, followed by Al-HIPIMS/V-HIPIMS, and Al-HIPIMS/V-DC. This particular trend is a consequence of a lower deposition rate for targets driven in HIPIMS mode, as fraction of the sputtered metal-ion flux is back attracted to the target.⁴⁴ The effect becomes more severe with increasing target power density (corresponding to higher ionization) and for most metals 20-45 % of the DC rate can be expected for peak target current densities used in this work (0.84-1.18 A/cm²).⁴⁵

4.3. $V_{1-x}Al_xN$ film structure, composition, and morphology

The most representative sets of comparative XRD data for $V_{1-x}Al_xN$ films with similar Al content are shown in Fig. 1: (a) $x = 0.55$, Al/V-DC, (b) $x = 0.58$, Al-HIPIMS/V-DC, (c) $x = 0.57$, V-HIPIMS/Al-DC, and (d) $x = 0.60$, Al-HIPIMS/V-HIPIMS. These films are also chosen for detailed TEM studies (see Fig. 3 below). Both Al/V-DC $V_{0.45}Al_{0.55}N$ and V-HIPIMS/Al-DC $V_{0.43}Al_{0.57}N$ layers consist of a mixture of NaCl cubic and wurtzite phases. The 111 and 002 NaCl

structure diffraction peaks recorded at the strain-free angle ψ^* are shifted towards higher diffraction angles with respect to the reference VN powder patterns (e.g. $2\theta_{002} = 44.02^\circ$ vs. 43.70° for powder sample)⁴⁶ due to incorporation of smaller Al atoms into the cubic lattice. The lattice shrinkage is, however, much smaller than in the case of well-studied TiAlN system,²⁰ due to significantly lower lattice constant of VN (4.139 Å) with respect to that of TiN (4.242 Å).⁴⁷ The relaxed lattice parameter a_o extracted from the 002 peak position is 4.116 Å for Al/V-DC $V_{0.45}Al_{0.55}N$ and 4.119 Å for V-HIPIMS/Al-DC $V_{0.43}Al_{0.57}N$; both somewhat lower than the bulk VN value. Simultaneously, the wurtzite phase $10\bar{1}0$ peak appears at lower 2θ angles as compared to the reference wurtzite AlN data⁴⁸ indicative of lattice expansion along the [100] axis caused by larger V atoms, from 3.111 Å for w -AlN to 3.180 Å in the case of Al/V-DC $V_{0.45}Al_{0.55}N$ and to 3.152 Å for V-HIPIMS/Al-DC $V_{0.43}Al_{0.57}N$ sample.

In distinct contrast, Al-HIPIMS/V-DC $V_{0.42}Al_{0.58}N$ and Al-HIPIMS/V-HIPIMS $V_{0.40}Al_{0.60}N$ films are single phase, with the NaCl structure, despite the higher Al content compared to films grown in the two other target configurations. Relaxed lattice parameters are 4.116 Å and 4.121 Å for Al-HIPIMS/V-DC and Al-HIPIMS/V-HIPIMS, respectively. In the latter case, 111 and 002 XRD reflections exhibit a very pronounced shift to higher 2θ angles with increasing ψ , indicative of very high compressive residual stresses (see Sec. 4.5 for more details).

The relative volume fractions χ of second phase w -AlN precipitates, estimated from NaCl phase 002 and wurtzite $10\bar{1}0$ peak intensities integrated over all ψ angles and normalized to random powder diffraction values, are plotted in Fig. 2 as a function of x for all four $V_{1-x}Al_xN$ film sets. In each case, there is a critical Al concentration value x_{max} , above which second phase is detected, corresponding to metastable solubility limit of AlN in the NaCl crystal lattice. Clearly, x_{max} exhibits large dependence on the particular choice of target powering configuration. The x_{max}

values obtained from the linear extrapolations of $\chi(x)$ data points towards the $\chi = 0$ axis reveal that the AlN solubility is lowest for the Al/V-DC configuration $x_{max} = 0.52$, followed by 0.55 for V-HIPIMS/Al-DC. Significantly higher values are achieved with Al-HIPIMS/V-DC, $x_{max} = 0.63$, and Al-HIPIMS/V-HIPIMS $x_{max} = 0.65$.

Typical fracture XSEM micrographs obtained from four sets of $V_{1-x}Al_xN$ alloy films with selected Al content are shown in Fig. S4 of the supplementary material. All films in the Al/V-DC series are characterized by columnar structure that is initially dense at lower x values ($x \leq 0.36$). With increasing Al content in the film ($0.55 \leq x \leq 0.72$) inter-columnar and intra-columnar porosity appears, a signature of low adatom surface mobilities.⁴⁹ In the case of hybrid Al-HIPIMS/V-DC growth film nanostructure evolves from dense columnar with $x \leq 0.29$ towards feature-less for $V_{1-x}Al_xN$ films with Al content $x \geq 0.58$. This is in contrast to films deposited with V-HIPIMS/Al-DC hybrid configuration exhibiting pronounced columns in the entire x range studied. In the latter case films are denser at lower x values ($x \leq 0.49$), with V-shaped columns indicative of competitive growth, and open up with increasing x , however, not to the level observed for Al/V-DC. The nanostructure evolution as a function of Al content in the case of purely HIPIMS $V_{1-x}Al_xN$ layers offers interesting observations. First, Al-HIPIMS/V-HIPIMS films with $x \sim 0.30$ are essentially identical to corresponding layers grown in the V-HIPIMS/Al-DC configuration, both column shape and surface topography are very similar. Secondly, with x increasing beyond 0.55, columnar morphology gradually disappears and Al-HIPIMS/V-HIPIMS films resemble high-Al-content layers grown in the Al-HIPIMS/V-DC configuration (see $x \gtrsim 0.60$ films in Fig.5), both exhibiting very fine grain size as confirmed by XRD peak broadening (not shown). Hence, both Al-HIPIMS/V-DC and Al-HIPIMS/V-HIPIMS films with $x \gtrsim 0.6$ are column-free which is in clear contrast to Al/V-DC and V-HIPIMS/Al-DC layers.

Figs. 3(a)-3(d) are bright-field XTEM images along with selected area electron diffraction (SAED) patterns (see insets) obtained from four $V_{1-x}Al_xN$ films with similar Al content: (a) $x = 0.55$, Al/V-DC, (b) $x = 0.58$, Al-HIPIMS/V-DC, (c) $x = 0.57$, V-HIPIMS/Al-DC, and (d) $x = 0.60$, Al-HIPIMS/V-HIPIMS. High porosity of the $V_{0.45}Al_{0.55}N$ Al/V-DC film observed with XSEM (Fig. S4) is evident especially in the high-magnification inset in Fig. 3(a). The average column width is 200 ± 20 nm, significantly higher than for $x = 0.58$ Al-HIPIMS/V-DC film (40 ± 10 nm), or $x = 0.57$ V-HIPIMS/Al-DC (35 ± 15 nm) and $x = 0.60$ Al-HIPIMS/V-HIPIMS (75 ± 25 nm) layers. SAED patterns from $V_{0.45}Al_{0.55}N$ Al/V-DC and $V_{0.43}Al_{0.57}N$ V-HIPIMS/Al-DC (Figs. 3(a) and 3(c)) films exhibits both cubic (111, 002, and 220) as well as wurtzite ($11\bar{2}0$ and $10\bar{1}0$) diffraction rings in agreement with XRD results shown in Figs. 1(a) and 1(c). In distinct contrast, for $V_{0.42}Al_{0.58}N$ Al-HIPIMS/V-DC and $V_{0.40}Al_{0.60}N$ Al-HIPIMS/V-HIPIMS layers (Fig. 3(b) and 3(d), respectively), single-phase NaCl structure, previously observed by XRD (Figs. 1(b) and 1(d)), is confirmed by electron diffraction. Both films have a dense columnar structure with no open boundaries, in agreement with XSEM in Fig. S4. $V_{0.40}Al_{0.60}N$ Al-HIPIMS/V-HIPIMS layer exhibits nanostructure characteristic of films grown by cathodic arc deposition.

The local chemical composition of selected $V_{1-x}Al_xN$ thin films was analyzed by atom probe tomography. In Fig. 4. the frequency distribution analysis of the majority components Al and VN detected during APT is displayed for (a) $x = 0.45$ Al/V-DC, and (b) $x = 0.58$ Al-HIPIMS/V-DC samples. The calculated binomial, random distribution data is plotted for comparison.

4.4. $V_{1-x}Al_xN$ nanoindentation hardness and elastic modulus

Fig. 5(a) shows elastic moduli $E(x)$ of $V_{1-x}Al_xN$ films grown by four powering configurations. In general, there is a very good correlation between $E(x)$ plots and XRD-determined metastable solubility limits (see Fig. 2). The measured elastic modulus for film with the lowest Al concentration, $E(x = 0.17) = 417 \pm 13$ GPa, is in excellent agreement with 417 GPa calculated in Ref. 29 for binary VN system. The onset of $E(x)$ decay takes place at $x \sim 0.50$ for both Al/V-DC and V-HIPIMS/Al-DC film series, which follow essentially the same trend. Above this critical Al content E drops from 415 ± 25 GPa obtained for layers with $x < 0.50$ to 310 ± 32 and 245 ± 36 GPa with $x = 0.56 \pm 0.01$ and $x = 0.62 \pm 0.02$, to saturate at 223 ± 28 GPa with $x \geq 0.70$. In the case of Al-HIPIMS/V-DC films, $E(x)$ does not decrease until $x = 0.64$, i.e., exactly at the same Al content where precipitation of w -AlN is detected (cf. Fig. 2). At this point drop from 398 ± 18 GPa with $x = 0.58$ to 331 ± 6 GPa is observed. For $V_{0.28}Al_{0.72}N$ Al-HIPIMS/V-DC film $E = 224 \pm 7$ GPa, which is very similar to elastic moduli of Al/V-DC and V-HIPIMS/Al-DC films in this composition range. Al-HIPIMS/V-HIPIMS series exhibits highest values for films with very high Al content ($x > 0.60$). In this case, $E = 428 \pm 12$ GPa with $x = 0.60$ and drops to 394 ± 6 , 353 ± 11 , and 312 ± 8 GPa with $x = 0.66$, 0.69 , and 0.72 .

The nanoindentation hardness $H(x)$, plotted in Fig. 5(b), exhibits general behavior similar to that of $E(x)$. For $x \lesssim 0.40$, $H(x)$ is essentially independent of the target configuration used and shows a slight increase from 27.7 ± 0.2 with $x = 0.17$ to 29 ± 1.6 GPa for $x = 0.40$. Increasing Al content beyond $x = 0.40$ reveals large dependence of $H(x)$ on the particular target configuration. For Al/V-DC a rapid decrease in H is observed, from 29.3 ± 1.3 GPa with $x = 0.41$ to 27.8 ± 1.5 , 22.4 ± 1.6 and 13.9 ± 2.0 GPa with $x = 0.45$, 0.51 and 0.55 . Films grown in a hybrid V-HIPIMS/Al-DC configuration exhibit high H values up to $x = 0.51$ (29.6 ± 1.8 GPa), after which hardness drops to 19.9 ± 1.3 GPa with $x = 0.57$ and stays at 14.7 ± 2.2 GPa for $x \geq 0.61$. In contrast,

softening takes place at much higher x if Al target (instead of V) operates in HIPIMS mode (Al-HIPIMS/V-DC) – reduction of H is not observed until $x = 0.64$ for which $H = 27.8 \pm 0.2$ GPa, followed by 20.3 ± 2.0 GPa with $x = 0.72$. In analogy to $E(x)$ data, for the Al-HIPIMS/V-HIPIMS case H remains very high, 30.7 ± 0.1 GPa, even with $x = 0.66$, after which a relatively slow decay takes place, first to 29.1 ± 0.6 GPa with $x = 0.69$, and then to 27.2 ± 0.8 GPa for $x = 0.72$.

The $H^3/E^2(x)$ ratio reflecting materials resistance against plastic deformation⁵⁰ and considered an important parameter describing mechanical properties of nanostructured thin films⁵¹ is plotted in Fig. 5(c) for $V_{1-x}Al_xN$ thin film alloys. Obviously, the observed behavior is a direct consequence of $H(x)$ and $E(x)$ trends described above. For Al/V-DC series, $H^3/E^2(x)$ curve drops off at $x \sim 0.45$, followed by V-HIPIMS/Al-DC ($x \sim 0.50$), and Al-HIPIMS/V-DC ($x \sim 0.64$). Interestingly for Al-HIPIMS/V-HIPIMS series, a continuous increase in $H^3/E^2(x)$ is observed from 0.12 with $x = 0.17$ to 0.21 with $x = 0.72$.

4.5. $V_{1-x}Al_xN$ residual stress

The enthalpies ΔH of cubic and wurtzite $V_{1-x}Al_xN$ in equilibrium as well as under a hydrostatic pressure of -6 GPa are shown in Fig. 6 as a function of x . ΔH values are calculated for configuration C#3 according to Mayrhofer et al.⁵ as this arrangement constitutes a compromise between the DC-deposited sample ($x = 0.45$) with a Pearson coefficient of 0.61 for VN, indicating clustering, and the HIPIMS-deposited sample ($x = 0.58$) with a Pearson coefficient of 0.06 for VN indicating a close to random distribution. As x is increased from 0 to 1, ΔH decreases from -1.012 to -1.303 eV/atom, and from -0.692 to -0.991 eV/atom, for c - $V_{1-x}Al_xN$ in equilibrium and under a hydrostatic pressure of -6 GPa, respectively. The calculated enthalpies of w - $V_{1-x}Al_xN$ decrease also as x is increased and cross the respective $\Delta H(x)$ plots for the cubic phases. The enthalpy of c -

$V_{1-x}Al_xN$ is lower for $x < 0.818$ and $x < 0.918$ in equilibrium and under a hydrostatic pressure of -6 GPa, respectively, compared to ΔH of w - $V_{1-x}Al_xN$, indicating that cubic phase is stable up to these Al concentrations. The change in maximum solubility limits Δx_{max} , expressed as a difference between x_{max} under hydrostatic pressure and at the equilibrium, are 0.032, 0.070, and 0.100 for applied hydrostatic pressures of -1.7, -4.0 and -6.0 GPa, respectively. Hence, it is evident that the critical solubility of Al in cubic phase is strongly pressure dependent. However, it is important to keep in mind that the here performed calculations describe the formation of two metastable ternary solid solutions, namely the cubic and the wurtzite phase. The experimental observation of the wurtzite phase at significantly lower x values than the critical x is due to energetics, as the thermodynamically stable binary wurtzite AlN phase (not the ternary solid solution) is energetically favored over the formation of metastable solid solutions.

Residual stress values $\sigma(x)$, obtained by the $\sin^2\psi$ method from the position of a 002 c - $V_{1-x}Al_xN$ Bragg reflection using the elastic moduli E values acquired from the nanoindentation measurements, are plotted in Fig. 7 for all $V_{1-x}Al_xN$ layers as a function of x . The pure DC configuration yields lowest $\sigma(x)$ values, which start from +0.1 GPa with $x = 0.32$ to peak at -1.6 GPa with $x = 0.41$ and gradually decrease again, so that nearly stress-free films are obtained with $x \geq 0.55$. For Al-HIPIMS/V-DC series, stresses are compressive and show a continuous increase with x , from -0.4 GPa with $x = 0.23$ to -1.3 and -1.6 GPa with $x = 0.4$ and 0.49, to eventually saturate at -2.7 GPa for $x \geq 0.58$. Entirely different trend is observed for V-HIPIMS/Al-DC $V_{1-x}Al_xN$ films in which case stresses are highly compressive even at low Al concentrations, $\sigma = -2.4$ GPa with $x = 0.23$, and increase further to reach a maximum of -3.4 GPa with $x = 0.39$, after which $\sigma(x)$ decays to -2.3, -1.6, and -0.4 GPa with $x = 0.51$, 0.57, and 0.64. Films grown in the Al-HIPIMS/V-HIPIMS configuration exhibit highest residual stresses of all powering schemes tested.

At lower Al content, $\sigma(x)$ is similar to values obtained for V-HIPIMS/Al-DC, with -2.5 GPa for $x = 0.17$ and increases rapidly to -3.5 GPa with $x = 0.33$ and -4.5 GPa with $x = 0.47$. For $0.50 \leq x \leq 0.60$, compressive stresses increase and reach the maximum at -5.2 GPa for $x = 0.66$, after which they decrease slightly to -4.5 GPa at $x = 0.69$.

5. Discussion

The results presented above reveal that $V_{1-x}Al_xN$ film structure, phase composition, mechanical properties, and residual stresses strongly depend on the processing strategy employed. One obvious difference when comparing metal target operation in DC *vs.* HIPIMS mode is the high ionization of the sputtered, film-forming, material flux characteristic for the latter technique,^{52,53} which is crucial, as the ion irradiation conditions during growth define film composition, structure, morphology, and, hence, properties. It is well established that the sputter-ejected species from metal targets operating in HIPIMS are readily ionized by electron impact in the dense plasma region due to low ionization potentials (relative to that of sputtering gas), provided that plasma density is high enough.⁵⁴ Typically, the ionization degree scales with the peak target current density.^{55,56} Hence, during HIPIMS, the growing film surface is exposed to pulsed ion irradiation for 10-20% of the deposition time, where metal-ions constitute a significant part of the total ion flux. In contrast, during DC, ionization of sputtered species is negligible, as film growth proceeds from neutrals and the ion irradiation is due to gas ions (primarily Ar^+ , N_2^+),⁵⁷ however, throughout the 100% of the deposition time. These differences allow for selection of a metal-ion type assisting the growth (Al^{n+} and/or V^{n+} , $n = 1, 2, \dots$) by simply choosing appropriate powering configuration (Al-HIPIMS/V-DC *vs.* V-HIPIMS/Al-DC *vs.* Al-HIPIMS/V-HIPIMS).

It was recently demonstrated that the average metal-ion charge state during HIPIMS is to large extent determined by the second ionization potential of a metal IP_{Me}^2 with respect to the first ionization potential of the sputtering gas IP_g^1 .⁵⁸ High doubly-ionized fraction of the sputtered metal flux can be expected if $IP_{Me}^2 < IP_g^1$, as is the case for V target sputtered in Ar/N₂ gas mixture ($IP_V^2 = 14.66$ eV, $IP_{Ar}^1 = 15.76$ eV, and $IP_{N_2}^1 = 15.55$ eV),⁵⁹ due to significant electron population with energies $IP_V^2 < E_e < IP_{N_2}^1$, *i.e.*, too low to ionize N₂, yet high enough to produce V²⁺. Hence, the metal-ion flux to the substrate is dominated by singly-charged ions if $IP_{Me}^2 > IP_g^1$, as for Al sputtered in Ar/N₂, for which $IP_{Al}^2 = 18.83$ eV, and gas ionization depletes the population of electrons with $E_e > IP_{Ar}^1$. Based on these arguments, both V⁺ and V²⁺ metal-ions can be expected during V-HIPIMS/Al-DC, while singly-charged Al⁺ ions should dominate metal-ion flux in the Al-HIPIMS/V-DC configuration.

During Al/V-DC processing, a continuous bombardment with ~100 eV gas ions (Ar⁺ and N₂⁺) enables surface diffusion of Al and V adatoms, which become mobile as recoils.²⁴ V and Al neutral fluxes together with the N₂ partial pressure determine film composition (neglecting resputtering and evaporation). As long as V flux dominates over that of Al, *c*-VN prevails on the surface providing a template for minority Al atoms that are incorporated into the cubic phase resulting in formation of metastable VAlN. 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 for V_{1-x}Al_xN films with $x > x_{max} = 0.52$ (cf. Fig. 2), in a very good agreement with the previously reported value of 0.54 obtained with a DC process employing substrate rotation and significantly shorter target-to-substrate distance.⁶⁰ The consequences of such growth conditions for the evolution of the spatially resolved chemical composition are revealed here by atom probe tomography (see Fig. 4). The frequency distribution analysis for the $x = 0.45$

Al/V-DC sample shows clear evidence for clustering of Al and V (Fig. 4(a)), as the Pearson coefficient is far from 0 which would indicate a random distribution. Hence, both elements exhibit a clear tendency to segregation, which facilitates precipitation of the w -AlN phase once Al concentration prevails over that of V ($x > 0.5$). Dense morphologies are obtained only at lower $x \leq 0.45$ (see Fig. S4). With increasing x , the growth rate increases rapidly while the ion flux incident at the growing film surface remains constant, resulting in a 3-fold decrease in J_i/J_{Me} (see Fig. S2). This is the primary reason for the evolution of the porous morphology of $V_{1-x}Al_xN$ layers with $x \geq 0.51$ (see Fig. S4 and Fig. 3(a)). Similar nanostructure evolution, from dense at lower x to porous at high Al content, was observed for VAlN layers grown by a combination of DC and mid-frequency (MF) magnetron sputtering.⁶¹

During sputter deposition in the hybrid Al-HIPIMS/V-DC and V-HIPIMS/Al-DC configurations, the film growth surface is subject to an intense high-energy ($V_s = -100$ V) metal-ion flux during the 200- μ s-long HIPIMS substrate bias pulses, and a continuous flux of low-energy (~ 10 eV) gas ions (Ar^+ , N_2^+ , and N^+) in the DC phase when the substrate is at floating potential. Since the latter energies are below the lattice displacement threshold (~ 20 -50 eV depending upon the ion and film species involved), the film structure evolution is determined mainly by the energy and momentum transfer due to metal-ion irradiation in the HIPIMS phase which is active during 10% of the deposition time.

Importantly, the film growth rates in the hybrid process are such that the total metal deposition between HIPIMS pulses corresponds to a fraction of a monolayer ($< 5 \times 10^{-3}$ ML). The effective depth of collision cascades (subplantation depth) is estimated from Monte-Carlo based TRIM simulations of ion/surface interactions,^{62,63} to be ~ 10 Å. Consequently, DC-deposited material is affected by several thousands of HIPIMS pulses before it is buried under the near-

surface region where subplantation takes place. Hence, it is reasonable to discuss the ion irradiation effects on the nanostructure evolution using the time-averaged J_i/J_{Me} values, rather than temporal, HIPIMS ion flux intensities.

Interestingly, there is a large difference in the Al solubility limits encountered between Al-HIPIMS/V-DC and V-HIPIMS/Al-DC configurations (see Fig. 2). This observation is even more striking given the fact that the J_i/J_{Me} in the relevant concentration range, $0.55 \leq x \leq 0.63$, is similar for $V_{1-x}Al_xN$ layers grown by both methods (see Fig. S2). The essential difference between the two hybrid scenarios is the fact that only during Al-HIPIMS/V-DC growth Al arrives at the film surface predominantly in the ionized state and is accelerated by the synchronous substrate bias. Al^+ ions with energy of ~ 100 eV are subplanted into the film, below the high-mobility surface zone, and become incorporated into the cubic VN grains formed by the continuous flux of low-energy V neutrals from the magnetron operating in DC mode. The resulting solubility limit, $x_{max} = 0.63$, is 12% higher than what can be explained based on the compressive stress of -2.8 GPa (see Fig.7). The results of *ab initio* calculations (Fig. 6) reveal that only 40% of the experimentally observed enhancement in solubility limit is caused by stress. The remaining 60% appear to be due to subplantation.

The frequency distribution analysis of the $x = 0.58$ Al-HIPIMS/V-DC sample grown with a synchronous substrate bias of -100 V (Fig. 4(b)) indicates Pearson coefficients close to 0, hence, Al and V are randomly distributed on the metal sublattice sites. This result can be rationalized by the fact that during Al-HIPIMS/V-DC growth scenario Al and V species are not allowed to coexist at the very surface where mobility is high, leading unavoidably to segregation. Instead, film-forming species are separated in time and energy domains. The V atoms deposited between HIPIMS pulses (90% duty cycle) are irradiated by the low-energy (~ 10 eV) gas ions which results

in surface diffusion and formation of cubic V-rich $V_{1-x}Al_xN$ crystallites, where the minority Al fraction stems from the non-ionized portion of the Al-HIPIMS flux. The ionized part of the Al flux (~ 100 eV, 10% duty cycle) is subplanted below the high-mobility surface zone and into the cubic V-rich $V_{1-x}Al_xN$ matrix to trigger local mobility on cation lattice and subsequent quenching, thus enabling the here reported enhancement in metastable solid solubility. 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. The latter is evidenced by the lack of Al and V clustering during Al-HIPIMS/V-DC in contrast to surface-diffusion-enabled Al and V clustering observed for DC films (see Fig. 4(a)). This, together with larger molar volume of w -AlN compared to c -AlN, hinders precipitation of the wurtzite AlN in the bulk, resulting in supersaturated c -VAlN. The scenario is valid as long as the incident V atom flux prevails over the non-ionized portion of the Al-HIPIMS flux, which assures that cubic $V_{1-x}Al_xN$ with $x < 0.5$ forms at the surface. Hence, the degree of Al ionization is decisive for how much the solubility limits can be increased above the conventionally-achieved levels.

For V-HIPIMS/Al-DC $V_{1-x}Al_xN$ films, detrimental ion bombardment effects at low x , where J_i/J_{Me} is high (cf. Fig. S2), lead to a similar nanostructure as that of Al-HIPIMS/V-HIPIMS layers (Fig. S4), and high residual stress of -3 ± 0.5 GPa. As x is increased, the formation of energetically-favored wurtzite phase takes place at $x = 0.55$, which is only marginally higher than in the Al/V-DC case. In fact, the actual increase in x_{max} with respect to the conventional DC processing, is exactly as predicted by *ab initio* calculations for the corresponding increase in σ , which is rationalized by the fact that during V-HIPIMS/Al-DC Al subplantation, as discussed above, is not active.

$V_{1-x}Al_xN$ films grown in the Al-HIPIMS/V-HIPIMS configuration are subject to the most

intense ion irradiation as indicated by high J_i/J_{Me} values in the entire x range (Fig. S2). Both Al^+ and V^+/V^{2+} irradiation is present (gas-ion bombardment between HIPIMS pulses is absent), however, since there is a random phase shift between Al-HIPIMS and V-HIPIMS pulses, the spatial density of collision cascades is not significantly higher than during hybrid process. The concentration of Al accommodated in the NaCl structure is highest of all powering schemes tested, $x = 0.65$. 60% of the increase in x_{max} is, however, due to large increase in compressive stresses (-4.6 vs. -2.8 GPa for Al-HIPIMS/V-DC) caused in turn by significantly higher ion irradiation damage ($J_i/J_{Me} = 4$ for Al-HIPIMS/V-HIPIMS vs. 2.2 for Al-HIPIMS/V-DC, both at corresponding value of x_{max}). $V_{1-x}Al_xN$ layers grown by pure HIPIMS process resemble ternary nitride films grown by cathodic arc, where high fluxes of multiply-charged metal-ions are present,⁶⁴ which yield high solubility limits and extremely high compressive stresses.⁶⁵

The effects of various types of metal ion bombardment explored in this work on Al solubility in cubic phase as well as on compressive stress relative to that of Al/V-DC, are schematically summarized in Fig. 8 for all $V_{1-x}Al_xN$ film sets. The dashed line indicates the *ab initio* calculated stabilization of the cubic phase for a given σ . For V-HIPIMS/Al-DC an experimentally determined x_{max} is exactly as expected based on the increase in the compressive stress value (-1.9 GPa at $x_{max} = 0.55$). This is in contrast to Al-HIPIMS/V-DC film growth, where Al^+ subplantation mechanism raises solubility such that x_{max} is clearly higher than expected based on the stress-induced stabilization alone for $\sigma = -2.8$ GPa (see Fig. 8). This indicates the crucial role of the subplantation effect which accounts for 60% of the increase in x_{max} . The Al-HIPIMS/V-HIPIMS result ($\sigma = -4.6$ GPa) with 40% contribution of subplantation effect to higher x_{max} , places this growth scenario between that of Al-HIPIMS/V-DC and V-HIPIMS/Al-DC, as could be intuitively predicted for the superposition of two HIPIMS sources. Higher value of

x_{max} for Al-HIPIMS/V-HIPIMS (0.65) than in the case of Al-HIPIMS/V-DC (0.63) is a result of much higher compressive stress in the former case.

The Al subplantation during Al-HIPIMS/V-DC can further be enhanced by increasing energy of incident metal ions (resulting in larger subplantation depth) and fine-tuning the synchronous bias pulse to the metal-rich portion of the HIPIMS discharge (for better separation of metal- and gas-ion fluxes).²⁴ We recently demonstrated Al solubility limit in VAlN as high as 0.75 by using 70-100 μ s long bias pulses with -300 V amplitude.²⁴ This data point is also included in Fig. 8 for comparison. Based on the results of *ab initio* calculations, it can be concluded that in this case the subplantation accounts for as much as 70% of the increase in x_{max} .

We note also that for all four growth scenarios tested here, there is a very good correlation between VAlN film phase content and mechanical properties (see Fig. 5). In particular, a rapid drop in elastic modulus correlates very well to corresponding x_{max} values. This is very interesting given the fact that apart from the phase content, E is also affected by morphology, chemical composition, and residual stress, all of which are varying in a wide range.

The here presented data clearly illustrate 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 solubilities in transition metal alumina nitrides with low or moderate compressive stress states. Hardness and elastic moduli of Al-HIPIMS/V-DC $V_{1-x}Al_xN$ films remain high, at respectively ~ 30 and ~ 420 GPa, in a wide compositional range. Thus, a substantial improvement of high temperature oxidation resistance can be expected without risking coating failure due to high compressive stresses, which is a significant advantage over conventional processing methods.

6. Conclusions

Metastable cubic $V_{1-x}Al_xN$ ($0.17 \leq x \leq 0.74$) alloy thin films were grown using co-sputtering in mixed Ar/N₂ discharges employing targets operating in DC and/or HIPIMS modes to appraise the effect of different metal ion irradiation conditions as well as the stress state on the critical Al solubility in the cubic matrix. Detailed correlative analysis of the experimentally obtained Al solubility limits x_{max} with the ion-irradiation-induced compressive film stresses σ , as well as with the results of *ab initio* calculations depicting the influence of σ on x_{max} , allows for separating between the contributions from stress and subplantation to the metastable Al supersaturation in $V_{1-x}Al_xN$.

We conclude that, in the case of V^+/V^{2+} irradiation (V-HIPIMS/Al-DC), the experimentally determined increase in solubility limit to $x_{max} = 0.55$ is entirely caused by stress-induced stabilization of the cubic phase. In contrast, Al^+ ion fluxes during Al-HIPIMS/V-DC provide a substantial increase in x_{max} to 0.63, which is 12% higher than expected based on the calculated stress-induced increase in metastable solubility. Based on atom probe tomography data, we infer that this solubility enhancement is enabled by Al subplantation active during 10% of the deposition time. $V_{1-x}Al_xN$ films grown in the Al-HIPIMS/V-HIPIMS configuration are subject to the most intense metal-ion irradiation. The relative gain in solubility for a corresponding increase in compressive stress places this growth scenario between that of V-HIPIMS/Al-DC and Al-HIPIMS/V-DC. x_{max} is highest of all methods at 0.65, this comes however at the steep price of very high compressive stress (-4.6 GPa).

Our results indicate that the Al-HIPIMS/V-DC configuration enables Al^+ subplantation causing a significantly enhanced Al solubility at moderate compressive stress owing to the separation of film-forming species in time and energy domains. Thus, a substantial improvement

of high temperature oxidation resistance can be expected without risking coating failure due to high compressive stresses, which is a significant advantage over state-of-the-art processing methods.

7. Supplementary Material

See supplementary material for target voltage and target current waveforms, time-averaged ion-to-metal flux ratios J_i/J_{Me} , relative Al content as a function of Al-to-V target time-averaged power ratio P_{Al}/P_V , representative cross-sectional SEM images, and typical strain vs. $\sin^2\psi$ plots for selected $V_{1-x}Al_xN$ films.

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Figure captions

- Fig. 1. XRD θ - 2θ scans as a function of the tilt angle ψ for (a) $x = 0.55$ Al/V-DC, (b) $x = 0.58$ Al-HIPIMS/V-DC, (c) $x = 0.57$ V-HIPIMS/Al-DC, and (d) $x = 0.60$ Al-HIPIMS/V-HIPIMS $V_{1-x}Al_xN$ films. “S” denotes the forbidden 002 reflection from the Si substrate, which appears due to multiple scattering.
- Fig. 2. $10\bar{1}0$ w-AlN and 002 NaCl c-VN peak area ratios integrated over all ψ angles and normalized to random powder XRD patterns plotted as a function of x for $V_{1-x}Al_xN$ films grown in four target powering configurations. The critical Al solubilities x_{max} are obtained by extrapolation.
- Fig. 3. Bright-field XTEM images together with corresponding SAED patterns for: (a) $x = 0.55$ Al/V-DC, (b) $x = 0.58$ Al-HIPIMS/V-DC, (c) $x = 0.57$ V-HIPIMS/Al-DC, and (d) $x = 0.60$ Al-HIPIMS/V-HIPIMS $V_{1-x}Al_xN$ layers.
- Fig. 4. Frequency distribution analysis of (a) $x = 0.45$ V/Al-DC, and (b) $x = 0.58$ Al-HIPIMS/V-DC $V_{1-x}Al_xN$ films, based on atom probe tomography data. Measured values for VN and Al are indicated by squares and circles and the calculated binomial distribution data is given as lines with corresponding color code. Pearson correlation coefficients μ are given for each species in brackets ($\mu = 0$ and 1 mean perfectly random and clustered distribution, respectively).
- Fig. 5. (a) Elastic moduli $E(x)$, (b) nanoindentation hardnesses $H(x)$, and (c) $H^3/E^2(x)$ ratios obtained from four sets of $V_{1-x}Al_xN$ films.
- Fig. 6. Enthalpies of the cubic (squares) and wurtzite (triangles) $V_{1-x}Al_xN$ in equilibrium (filled) and under a hydrostatic pressure of -6 GPa (open). The maximum Al solubility (x_{max}) in cubic $V_{1-x}Al_xN$ is depicted for the equilibrium case (black circle) and under a hydrostatic pressure of -1.7 GPa (red square), -4 GPa (green pentagon) and -6 GPa (blue triangle).
- Fig. 7. Residual stress $\sigma(x)$ obtained from four sets of $V_{1-x}Al_xN$ films. Vertical dashed lines indicate the corresponding x_{max} values.
- Fig. 8. An increase of the Al solubility limit Δx_{max} with respect to the Al/V-DC x_{max} value of 0.52, plotted as a function of the residual compressive stress σ for all four sets of $V_{1-x}Al_xN$ films. In addition, a film deposited at -300 V synchronous bias pulse fine-tuned to the metal-rich portion of the HIPIMS discharge (for better separation of metal- and gas-ion fluxes) is included for comparison. A dashed line indicates the calculated

stress-stability line. Numbers in brackets indicate the relative contribution of the subplantation to the stabilization of cubic phase.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Al/V-DC

Al-HIPIMS/V-DC

V-HIPIMS/Al-DC

Al-HIPIMS/V-HIPIMS

200 nm

Fig. S5

Fig. S1

Fig. S2

Fig. S3

Fig. S1

Fig. S1 Target voltage and target current waveforms recorded during the 50-μs-long Al-HIPIMS/V-DCMS discharge.

Fig. S2

Fig. S2 Time-averaged ion-to-metal flux ratios measured at the substrate position for all four target configurations tested.

Substrate ion saturation current density J_s estimates are based on the assumptions that (i) majority of the substrate current is collected by the substrate plate ($120 \times 310 \text{ mm}^2$), and (ii) the edge effects can be neglected due to large effective area of the substrate plate. This procedure is justified by the fact that it is the relative difference between J_s recorded in different target configurations that are of interest here, rather than the absolute current density values.

The time-averaged ion/metal flux ratios J_i/J_{Me} are directly obtained from J_s and film growth rates, neglecting resputtering effects.

Fig. S3

Fig. S3 Relative Al content $x = Al/(Al+V)$ in $V_{1-x}Al_xN$ films grown by Al-HIPIMS/V-DC, V-HIPIMS/Al-DC, and Al-HIPIMS/V-HIPIMS as a function of Al-to-V target time-averaged power ratio P_{Al}/P_V .

Fig. S4 Most representative cross-sectional SEM images obtained from four sets of $V_{1-x}Al_xN$ alloy films with selected Al content. Columns from left to right correspond to Al/V-DC, Al-HIPIMS/V-DC, V-HIPIMS/Al-DC, and Al-HIPIMS/V-HIPIMS layers. XRD-determined phase composition is also indicated for each film.

Fig. S5

Fig. S5 Typical strain *vs.* $\sin^2 \psi$ plots for selected $V_{1-x}Al_xN$ films: (a) $x = 0.55$ Al/V-DC, (b) $x = 0.58$ Al-HIPIMS/V-DC, (c) $x = 0.57$ V-HIPIMS/Al-DC, and (d) $x = 0.60$ Al-HIPIMS/V-HIPIMS.

Residual stress values σ were obtained from $\sin^2 \psi$ analyses as a function of film composition x for all four $V_{1-x}Al_xN$ film series. For this purpose, film strain ε was evaluated by measuring the position of a Bragg reflection to obtain the corresponding film interplanar spacing d as a function of the tilt angle ψ between the sample normal and the scattering plane defined by incoming and diffracted x-ray beams. The film strain ε as a function of the tilt angle ψ , defined with respect to the substrate normal, is equal to the normalized difference between d and the relaxed interplanar spacing d_o ,

$$\varepsilon(\psi) = \frac{d - d_o}{d_o}. \quad (1)$$

Measured $\varepsilon(\psi)$ values were used to determine the residual stress σ through Hooke's law of linear elasticity as:

$$\varepsilon(\psi) = \frac{1+\nu}{E} \sigma \sin^2 \psi - \frac{2\nu}{E} \sigma, \quad (2)$$

where ν is Poisson's ratio and E is the elastic modulus. Experimentally, the in-plane stress was extracted from the slope of $\varepsilon(\psi)$ vs. $\sin^2 \psi$. Figure S5 shows strain vs. $\sin^2 \psi$ plots for selected $V_{1-x}Al_xN$ films: (a) $x = 0.55$ Al/V-DC, (b) $x = 0.58$ Al-HIPIMS/V-DC, (c) $x = 0.57$ V-HIPIMS/Al-DC, and (d) $x = 0.60$ Al-HIPIMS/V-HIPIMS. The difference in the slope and sign of the curves reflects the type, compressive vs. tensile, of residual stress in the layers.