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ORIGINAL REPORT

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Unprecedented thermal stability of inherently metastable titanium aluminum nitride by point defect engineering

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ABSTRACT

Extreme cooling rates during physical vapor deposition (PVD) allow growth of metastable phases. However, we propose that reactive PVD processes can be described by a gas–solid paraequilibrium defining chemical composition and thus point defect concentration. We show that this notion allows for point defect engineering by controlling deposition conditions. As example we demonstrate that thermal stability of metastable (Ti,Al)N_x, the industrial benchmark coating for wear protection, can be increased from 800°C to unprecedented 1200°C by minimizing the vacancy concentration. The thermodynamic approach formulated here opens a pathway for thermal stability engineering by point defects in reactively deposited thin films.

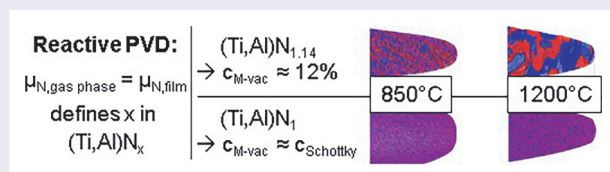
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TiAlN; thin films; hard coatings; vacancies; thermodynamics



IMPACT STATEMENT

A novel thermodynamic methodology to predict stoichiometry of coatings is utilized to increase thermal stability of today's industrial benchmark hard coating TiAlN from 800°C to 1200°C by point defect engineering.

Introduction

Generally, thermodynamically stable phases are employed in high-temperature applications. Thin film (Ti,Al)N is one exception to the rule. Since the first report 30 years ago [1], (Ti,Al)N has replaced TiN [2,3] as industrial benchmark hard coating due to the excellent mechanical properties and an increase of ~250°C in oxidation temperature [1,4–8]. In the last two decades it was understood that spinodal decomposition into TiN and AlN is caused by the extreme driving force for de-mixing on the metal sublattice of the cubic NaCl structure [4–7]. The cubic AlN-rich domains then phase transform at ~1000°C into thermodynamically stable hexagonal wurtzite-AlN. The concurrent volume increase leads to cracking and failure of the protective coating, thus ultimately limiting lifetime and performance of the coating [4,6,9–14].

Defects in (Ti,Al)N have recently gained considerable interest. Alling et al. have studied the effect of nitrogen vacancies on the decomposition energetics of (Ti,Al)N_x ($x \leq 1$) [15]. Baben et al. have shown theoretically that metal and nitrogen vacancies are the defects with the lowest energy of formation to accommodate off-stoichiometry [16]. Grönghagen et al. have used a rudimentary thermodynamic description of (Ti,Al)N_x ($x \geq 1$) based on an arbitrarily chosen metal vacancy concentration in a Cahn–Hilliard model and calculated faster decomposition kinetics with larger vacancy concentration [17]. Considering the large number of papers describing synthesis and properties of (Ti,Al)N and the technological importance of this coating system, it is astonishing that no reports are available describing the effect of nitrogen content on thermal stability. The accurate measurement of the (Ti,Al)N_x stoichiometry

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is prerequisite to a meaningful discussion of the defect structure and will provide information on what point defects (metal versus nitrogen vacancies) are actually present in as-deposited (Ti,Al)N. Therefore, the relationship between stoichiometry, presence and nature of point defects and the consequence thereof for the spinodal decomposition present experimentally uncharted territory.

Figure 1(a) shows a schematic of conventionally employed reactive magnetron sputtering: the reactive gas, in this case N_2 , is introduced in the deposition chamber homogeneously in order to obtain constant product quality over the whole deposited area. The high flow of nitrogen leads to poisoning of the metal target, meaning that a nitride covers the target surface and has to be sputtered. The vapor that interacts with the growing film therefore consists of metals and atomic and molecular nitrogen. Part of the vapor is ionized and there is a high partial pressure of inert sputtering gas. While the reactive sputtering process is on a global level rather well understood [19,20], there is no theory available that describes (off-) stoichiometry, that is, the nitrogen-to-metal ratio N/M of the thin film.

Here, we utilize a newly developed combinatorial deposition setup using reactive gas gradients to continuously vary the nitrogen-to-metal ratio N/M in the thin film [21]. As shown schematically in Figure 1(b), the nitrogen gas inlet is placed at the short side of the

rectangular magnetron. The nitrogen flow is chosen sufficiently small as to poison the target only partially in the target region in the vicinity of the gas inlet. Consequently, a nitrogen partial pressure gradient forms along the long axis of the magnetron (top to bottom in Figure 1(b)): close to the gas inlet the vapor that interacts with the growing film contains a high nitrogen partial pressure which decreases with increasing distance from the inlet. This method allows for the synthesis of thin films with a systematically changed N/M ratio or stoichiometry x in (Ti,Al) N_x along the long axis of the magnetron in a single deposition run. Therefore, the deposited film exhibits continuously varying concentrations of metal vacancies c_{M-vac} and nitrogen vacancies c_{N-vac} . While a direct measurement of the nitrogen partial pressure during reactive gas combinatorics in an industrial growth system presents a formidable challenge, the fact that the deposition geometry displayed in Figure 1(b) will result in the formation of a reactive gas partial pressure gradient along the long axis of the rectangular magnetron remains undisputed.

Depositing (Ti,Al) N_x with $x > 1$, $x \approx 1$ and $x < 1$, we show that the already surprisingly large thermal stability of metastable (Ti,Al)N can be further increased by 400°C using point defect engineering. Avoiding previously unidentified nitrogen overstoichiometry, a reduction in metal vacancy concentration by 12 orders of magnitude compared to thin films studied and employed

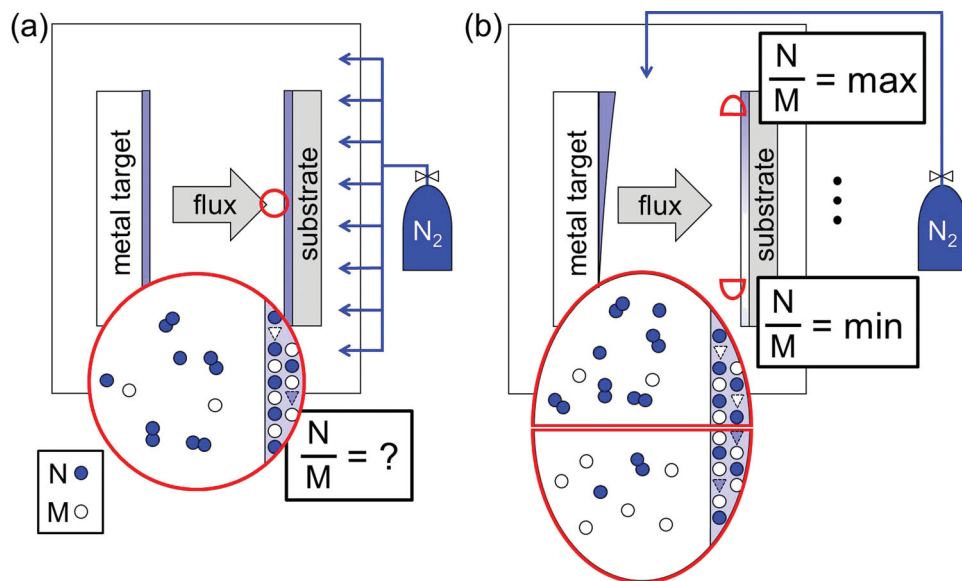


Figure 1. Schematics of reactive PVD. (a) Sputtering a metal target in poisoned mode. The reactive gas (here: N_2) is inserted homogeneously into the chamber; on the metal target a nitride forms; the vapor that interacts with the film consists of metal and nitrogen atoms as well as a large amount of nitrogen molecules (inset). To date, there is no theory available that describes the nitrogen-to-metal ratio N/M of the thin film. (b) Combinatorial deposition setup using reactive gas gradients [18]; the reactive gas is inserted at one end of the metal target. Close to the gas inlet, a nitride forms on the metal target and there is a large N_2 -partial pressure (upper inset). With increasing distance, the nitrogen partial pressure decreases and finally a metal is deposited (bottom inset). The stoichiometry and therefore concentrations of metal and nitrogen vacancies are continuously varied in the thin film.

industrially in the last decades is here identified to be responsible for the decrease in diffusivity, which is directly proportional to metal vacancy concentration. It should be noted that we distinguish two populations of point defects in nitride films: one population accommodates off-stoichiometry and another is generated due to the rapid quenching and energetic particle bombardment (here referred to as growth defects). Only the latter annihilate during annealing while the first do not. Therefore, the defects accommodating off-stoichiometry influence diffusivity at high temperature. We do not assume excess nitrogen to be primarily incorporated due to ion bombardment [22] but argue that the stoichiometry of reactively grown films can be estimated based on thermodynamic considerations: the high nitrogen partial pressure conventionally employed during reactive physical vapor deposition (PVD) of (Ti,Al)N leads to growth of slightly nitrogen overstoichiometric films due to a paraequilibrium between nitrogen in the gas phase and the film surface during growth. Paraequilibrium [23] implies that only the chemical potential of one selected element is equal in all phases while the contents of the other elements are fixed. In our case Ti and Al are set to fixed amounts in a single solid phase that are determined based on their condensation rates. On the other hand, the nitrogen content in the solid is defined by equal chemical potential of nitrogen in the solid phase and the vapor at given pressure, $\mu_{\text{N,film}} = \mu_{\text{N,gas phase}}$. Decomposition of (Ti,Al)N into the thermodynamically stable phases TiN and AlN during growth is kinetically hindered since metal diffusion over the length scale of many tens or even hundreds of atomic distances [24] is required. Hence, to enable diffusion metal atoms need to overcome an activation energy in the order of one electronvolt many tens or even hundreds of times [24,25]. Nitrogen adsorption and desorption on the other hand are single-step processes with activation energy in the same order of magnitude [26,27]. The nature of point defects that accommodates off-stoichiometry during growth remains unknown. Certainly, off-stoichiometry is predominantly accommodated by vacancies due to their low formation energy [16] after annealing at intermediate temperatures: growth defects were reported to annihilate [22,28] before massive diffusion of Ti and Al over a length of nm occurs: for growth defect annihilation few atomic movements are needed while for massive diffusion tens or hundreds of atomic movements are required. This reasoning is supported by temperatures around 700°C reported for point defect annihilation in (Ti,Al)N [4,11].

The here proposed existence of a paraequilibrium between the gas phase and the film during synthesis is the basis for a first theory to describe stoichiometry and hence defect formation besides growth defects of all

reactively deposited thin films: Even though it is accepted that the extreme quenching rates ($\sim 10^{15}$ K/s: from metal vapor to solid within fs [29]) allow for growth of thermodynamically metastable phases [22,30], (Ti,Al)N being an excellent example [6,23,31], we propose that the amount of incorporated nitrogen is defined by a paraequilibrium between nitrogen in the gas phase and in the metastable film surface during growth, $\mu_{\text{N,gas phase}} = \mu_{\text{N,film}}$. Based on the gas–solid paraequilibrium notion we introduce a methodology utilizing defect energies from *ab initio* calculations for thermodynamic calculations, allowing stoichiometry and thus point defect concentrations remaining after healing out growth defects by annealing [22,28] of reactively grown films to be predicted.

While modelling and hence predicting all processes in vapor phase condensation remains a task that is beyond current computational ability, point defect concentrations can now be tuned by controlling stoichiometry during reactive PVD and post-deposition annihilation of growth defects, and hence properties can be tailored, for example, for applications as electronic [32,33], transparent conductive [34], electrochromic [35] or hard films.

Calculations details

The Vienna *ab initio* simulation package was used to perform density functional theory [36] calculations of (Ti,Al)N_x. Generalized-gradient approximation-based projector augmented wave potentials [37], reciprocal-space integration with a Monkhorst–Pack scheme [38], the tetrahedron method with Blöchl-corrections for the total energy [39], a *k*-points grid of $6 \times 6 \times 6$, 0.01 meV electronic relaxation convergence and energy cutoff of 500 eV were used for the calculations. Additionally to the described defect structures in a previous paper [16], here we have calculated the energy of formation of a $2 \times 2 \times 2$ (Ti_{0.5}Al_{0.5})N_x supercell with only one Ti or one Al vacancy. The resulting total energies were averaged in order to determine the total energy of a $2 \times 2 \times 2$ supercell containing half a Ti and half an Al vacancy. For comparison with available thermodynamic data, energy of formation of TiN_x and AlN_x was calculated using the same parameters as for Ti_{0.5}Al_{0.5}N_x. Ideal configurations and configurations containing 2 and 4 vacancies were considered, respectively.

The energy barrier for the atomic jumps $E_{\text{M-vacancy-jump}}$ has been calculated by dragging a Ti or Al atom from a normal lattice site into an adjacent vacancy site in a $2 \times 2 \times 2$ supercell containing one Ti and one Al vacancy. During this, the lattice positions of the two metal atoms with maximum distance from the moving atom were fixed while all other atoms were allowed to relax.

For thermodynamic calculations, the description used in the Scientific Group Thermodata Europe solutions database [40] for the fcc-solution was used as a basis. Details on the thermodynamic modelling can be found in the Supplementary Material. FactSageTM [41] was then used to calculate the chemical potential of nitrogen in $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}_x$ and the gas phase.

Experimental details

Nitrogen overstoichiometric ($x > 1$), stoichiometric ($x = 1$) and understoichiometric ($x < 1$) $(\text{Ti,Al})\text{N}_x$ thin films have been deposited in a single deposition process using a newly developed combinatorial setup based on gas phase combinatorics [18]. Thin films were grown in an industrial scale deposition system (CemeCon CC800/9) using a rectangular $500 \times 88 \times 10 \text{ mm}^3$ TiAl target. A gas inlet was installed at the short side of the rectangular magnetron (Figure 1(b)) [18], which was used to introduce N_2 while Ar was introduced homogeneously into the deposition system. Optical inspection of the target surface after sputtering indicated that the target was poisoned close to the nitrogen inlet while it was in metallic mode at the other end. Sapphire substrates were clamped on a $500 \times 120 \times 3 \text{ mm}^3$ substrate holder at a target-to-substrate distance of 45 mm that was heated to $\sim 300^\circ\text{C}$ and electrically floating at a potential of -25 to -35 V . The base pressure at deposition temperature was below 1 mPa. A Melec High Power Pulsed Magnetron Sputtering (HPPMS) generator (SIPP2000USB-10-500-S) was used with a frequency of 400 Hz, duty cycle of 3.2% and a time-average power of 2000 W resulting in peak power density of 0.3 kW/cm^2 . The Ar flow was 200 sccm and the N_2 flow 9 sccm, resulting in 380 mPa total pressure during deposition. The deposition time was 30 min.

For comparison, $(\text{Ti,Al})\text{N}_x$ was also deposited by sputtering a poisoned TiAl target [42]. A poisoned target surface is obtained by sputtering in a N_2 abundant atmosphere resulting in larger nitride formation rate than the nitride sputtering rate at the target, meaning that a nitride is sputtered rather than metals. Here we introduce a flow of N_2 of 50 sccm homogeneously into the deposition system, resulting in a N_2 partial pressure of 95 mPa. HPPMS was used with a frequency of 800 Hz, duty cycle of 4% and a time-average power of 3000 W resulting in peak power density of 0.4 kW/cm^2 . The deposition time on amorphous carbon substrates was 5 min and on sapphire 30 min, where the first samples were used to enable optimum Rutherford back-scattering spectrometry (RBS) measurements conditions while the second set was used for nanoindentation, thermal stability and atom probe investigations. In order to avoid

surface oxidation [43], all samples were cooled in vacuum and taken out of the deposition system only when the temperature was below 50°C .

The thin films were annealed in high vacuum for 30 min at temperatures between 800°C and 1200°C with a heating rate of $10\text{--}15^\circ\text{C/min}$.

The sample composition was quantified by RBS and Time-Of-Flight Elastic Recoil Detection Analysis (TOF-ERDA) in a standard-free method. Measurements were performed using the 5 MV Pelletron tandem accelerator at The Tandem Laboratory at Uppsala University. 2 MeV He^+ ions were employed for RBS and detected in a scattering angle of 170 degrees. Recoil particles were detected for a detection angle of 45 degrees directing a primary beam of 36 MeV I^{8+} ions on the sample under 67.5 degrees with respect to the surface normal. Details of the employed type of TOF-ERDA detector system are described elsewhere [44]. Data analysis was supported by the commercially available SIMNRA code [45] and the CONTES software package [46]. Of particular relevance for the present evaluation is the non-unity detection efficiency for the TOF-detector. The detection efficiencies for the species of interest, that is, Ti, Al, N and O are found slightly lower than unity, with values as low as 0.85 for the lightest species, that is, the material with the lowest energy deposition in the detector. A two-step calibration of the foil-detector efficiency for TOF-ERDA was performed. First, a primary beam of nitrogen was scattered from a thin film target and the respective count rates at the time and energy detection system were compared. In a second step, a thin film sample of $(\text{Ti,Al})\text{N}_x$ grown on C was analyzed using RBS and TOF-ERDA to further reduce systematic uncertainties to contributions from counting statistics and minor systematic uncertainties from scattering potentials only. Further information can be found in the Supplementary Material.

X-ray diffraction was used to study the structure using a Siemens D5000 diffractometer with $\text{Cu-K}\alpha$ radiation in an unlocked coupled setup detecting lattice planes that are tilted one degree with respect to the substrate surface in order to avoid detection of planes from the single crystalline substrates. X-ray stress analysis (XSA) was done following the theory developed by Genzel for $\langle 001 \rangle$ -textured cubic crystals [47]. The fitting was done according to our previous work [21] and the elastic compliance was taken from Tasnádi et al. [48].

Nanoindentation was carried out in a Hysitron TI-900 TriboIndenter and elastic modulus as well as hardness of thin films were determined by the method of Oliver and Pharr [49]. A Berkovich diamond tip ($E = 1140 \text{ GPa}$, $\nu = 0.07$, $r = 100 \text{ nm}$) was used in load-controlled mode and the maximum force of 8 mN resulted in contact depth values of $< 100 \text{ nm}$. Thirty-two indents were

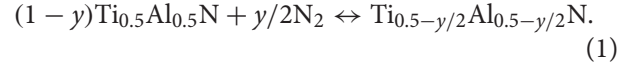
applied for each composition and each temperature, while the tip area function was determined with a fused silica standard. Elastic modulus values were calculated from reduced modulus with Poisson's ratio of $\nu = 0.214$ [17].

Compositional distributions of Ti, Al and N were investigated by 3D Atom Probe Tomography (3D-APT) in a CAMECA LEAP 4000X HR employing laser pulse-assisted field evaporation with 250 kHz frequency, 30 pJ laser energy and 60 K specimen temperature. 3D-APT specimens were prepared in a FEI HELIOS Nanolab 660 dual beam-focused ion beam microscope by a standard lift-out procedure and annular milling [50,51].

Results and discussion

During reactive deposition, nitrogen gas is present abundantly when working in the poisoned mode, that is, when the nitride formation rate at the target equals the nitride sputtering rate. Hence, assuming that the reaction of nitrogen with the growing film is not kinetically limited since nitrogen adsorption and desorption are single-step processes with activation energy in the order of one electronvolt [26,27], the nitrogen concentration will be determined by the driving force for the following chemical

reaction:



The driving force for N incorporation in $\text{Ti}_{0.5}\text{Al}_{0.5}\text{N}_x$ according to Equation (1) was determined by *ab initio* calculations and is shown in Figure 2(a) as function of metal vacancy concentration.

The driving force for N incorporation is negative for metal vacancy concentrations $c_{\text{M-vac}}$ smaller $\sim 10\%$ (metal vacancy concentration is here used with respect to available metal sublattice sites of the NaCl structure), showing a minimum around 6% of metal vacancies. Since the *ab initio* calculations were performed at 0 K, the calculated energy of formation was used as input for CALPHAD calculations [41] as described in the Supplementary Material. The resulting chemical potential of nitrogen in $(\text{Ti,Al})\text{N}_x$ is shown in Figure 2(b) and compared to that of pure nitrogen gas [52]. At a nitrogen partial pressure typically employed during reactive sputtering (10^{-6} bar as lower boundary), equilibrium between the gas phase and a single solid phase is obtained for a nitrogen-to-metal ratio x of 1.017, corresponding to a metal vacancy concentration $c_{\text{M-vac}}$ of 1.7% or a nitrogen content of 50.44 at%. Since the number

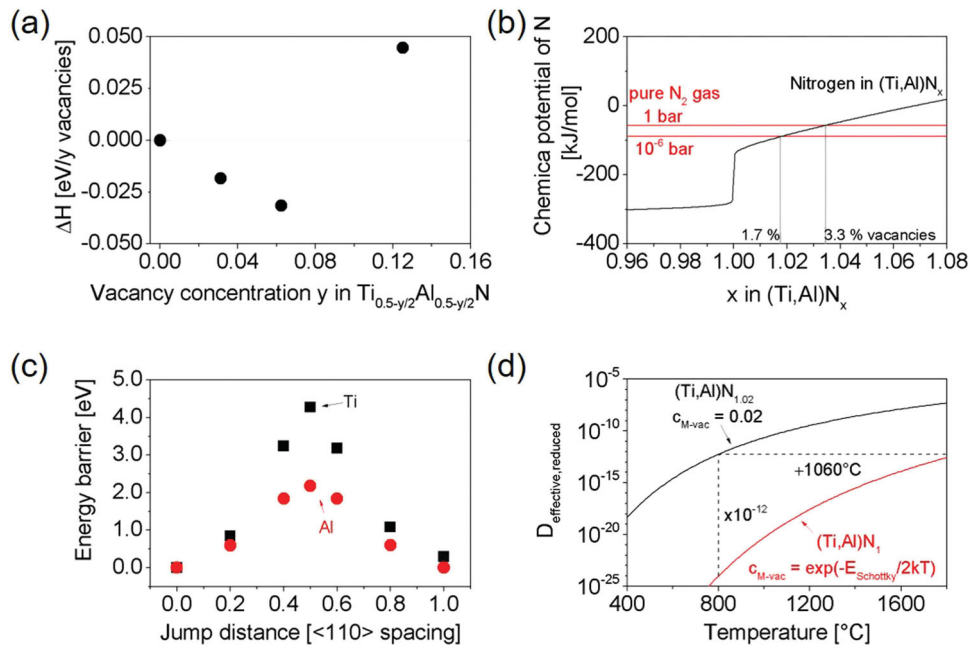


Figure 2. Theoretical results on energetics of defects and their mobility in $(\text{Ti,Al})\text{N}_x$. (a) Energy of reaction according to Equation (1). (b) Chemical potential of nitrogen as a function of nitrogen concentration in $(\text{Ti,Al})\text{N}_x$ at 300°C. Chemical potential of nitrogen as N_2 (gas) is included for 1 and 10^{-6} bar. Resulting equilibrium metal vacancy concentrations are indicated by grey lines. (c) Energy barrier for Ti and Al moving into an adjacent metal vacancy site in $(\text{Ti,Al})\text{N}_x$. (d) Effective reduced diffusion constant for metal diffusion in $(\text{Ti,Al})\text{N}_x$ depending on stoichiometry and hence the metal vacancy concentration $c_{\text{M-vac}}$.

Note: Dashed lines indicate how changing $c_{\text{M-vac}}$ from 2% to the Schottky defect concentration decreases diffusivity at 800°C and increases the temperature needed for the same diffusivity

of metal lattice sites is equal to the number of nitrogen atoms and the number of vacancies is equal to the difference between number of lattice sites and nitrogen content, c_{M-vac} and c_N are connected as follows:

$$\begin{aligned} c_{M-vac} &= (\text{Number of vacancies}) / \\ &(\text{Number of lattice sites}) \\ &= (c_N - [1 - c_N]) / c_N. \end{aligned} \quad (2)$$

During reactive PVD nitrogen is not only present as molecule but also as atomic, excited and ionic nitrogen [53] which exhibit a larger chemical potential and will hence further increase the metal vacancy concentration. Thus, by employing *ab initio* and CALPHAD calculations we predict that a few percent of the metal sites in $(Ti,Al)N_x$ are not occupied if state-of-the-art synthesis technology is employed where N_2 is present abundantly. These vacancies are important for thermal stability of metastable $(Ti,Al)N_x$ at higher temperatures since no energy for vacancy formation is needed for diffusion on the metal sublattice but only the activation energy for changing the atomic positions.

A mass loss of up to 3 wt% has been observed during thermogravimetric analysis of $(Ti,Al)N_x$ at 1200°C [13,14,54] due to N_2 evaporation [14]. Assuming that this leads to stoichiometric nitrogen content in the remaining film, the nitrogen content in as-deposited $(Ti,Al)N_x$ can be estimated as up to $x \approx 1.11$ resulting in $c_{M-vac} = 10\%$ which is in good agreement with the predicted metal vacancy concentration of few percent, considering that atomic, excited and ionic nitrogen is present during synthesis which will increase the metal vacancy concentration.

It should be noted that a thorough study of stoichiometry and hence metal vacancy concentration of $(Ti,Al)N_x$ thin films is missing in the literature and for arc-evaporated coatings not meaningful since the unavoidable formation of droplets [55] affect the composition measured by non-local techniques such as nuclear resonance analysis (NRA) or RBS. A state-of-the-art analysis of ZrN_x thin films deposited under nitrogen ion irradiation using NRA and RBS showed that the N/Zr ratio can change with deposition conditions between 1 and 1.8 [56]. Increasing the N/Zr ratio was observed with increasing nitrogen ion energy, which can be understood by considering that the chemical potential of ionic nitrogen is directly proportional to the ion energy.

In the following section, the impact of metal vacancy concentration on diffusivity and hence thermal stability will be quantified. In the literature, the activation energies reported for spinodal decomposition of $TiAlN$ are 3.4 [4] and 3.14 eV/atom [57], while diffusion constants used for

modelling the spinodal decomposition exhibit an activation energy of 1.9 eV/atom [58]. For stoichiometric $(Ti,Al)N_x$ ($x = 1$), assuming that growth-related defects are annihilated and defect concentration according to a Schottky equilibrium is reached, the activation energy for diffusion is $E_A(x = 1) = E_{Schottky}/2 + E_{M-vacancy-jump}$, where $E_{Schottky}$ is the energy of a Schottky defect and $E_{M-vacancy-jump}$ is the activation energy for a metal atom moving into a neighboring vacancy site. For nitrogen overstoichiometric $(Ti,Al)N_x$ ($x > 1$), the formation of Schottky defects is not needed and the activation energy is $E_A(x > 1) = E_{M-vacancy-jump}$. The energy barrier for a metal moving from one lattice site into an adjacent lattice site $E_{M-vacancy-jump}$ determined using *ab initio* calculations is shown in Figure 2(c).

The calculated activation energy for metal diffusion is 4.3 and 2.2 eV for Ti and Al, respectively. The magnitude of these values is on the same order as the formation energy of a Schottky defect, that is, the energy of formation of a metal vacancy plus a nitrogen vacancy, 5.72 eV [16,59]. Since the pre-exponential factor of the diffusion coefficient does not depend on the source of metal vacancies and requires significantly more effort to be determined theoretically [60], a reduced diffusion coefficient for metal ($M = Ti, Al$) diffusion is calculated using the metal vacancy concentration and the activation energy for atomic jumps only:

$$D_{reduced,M} = c_{M-vac} * \exp(-E_{M-vacancy-jump}/RT). \quad (3)$$

Using Darken's equation [61] the effective reduced diffusion coefficient can be calculated as follows:

$$D_{effective,reduced} = c_{Al} * D_{reduced,Ti} + c_{Ti} * D_{reduced,Al}. \quad (4)$$

In the following discussion, two cases are distinguished: first, $x = 1.02$, meaning a metal vacancy concentration of 2% is assumed, as predicted above, or and second as lower bound stoichiometric ($x = 1$) $(Ti,Al)N_x$ resulting in a metal vacancy concentration equal to the thermally induced metal vacancy concentration from Schottky defects [62]. The respective effective reduced diffusion coefficients are shown in Figure 2(d) as a function of temperature.

Since spinodal decomposition is taking place at $\sim 800^\circ\text{C}$ [4–6,9,10], the effective reduced diffusion coefficients are compared at this temperature. Decreasing the metal vacancy concentration from a constant value of 2% to the thermally induced vacancy concentration due to Schottky defects of 10^{-14} decreases the diffusivity by 12 orders of magnitude, see Figure 2(d). The temperature increase required to obtain the same order of magnitude in the effective reduced diffusion coefficient

as for the material with 2% metal vacancies is 1060°C, underlining the untapped potential of defect engineering for extraordinary thermal stability enhancements. This theoretical prediction will be evaluated in the following section experimentally.

In addition to the overstoichiometric $\text{TiAlN}_{1.1}$ sample obtained by sputtering a poisoned target three more films were deposited with precisely controlled N content, covering the range from over- to understoichiometric compositions. For this, reactive gas gradients were utilized in a newly developed combinatorial reactive magnetron sputtering setup [18]: a photograph of the TiAl target with the nitrogen gas inlet at the short side of the magnetron (left) is shown in Figure 3(a). During deposition, a nitrogen partial pressure gradient forms with decreasing nitrogen partial pressure with increasing distance from the gas inlet.

To obtain reliable chemical composition data, the composition of a thin film deposited on glassy carbon was measured by RBS to determine accurate detection efficiencies for ERDA. Further details can be found in the Supplementary Material. Chemical composition of thin films determined by ERDA as a function of distance from the N_2 gas inlet is shown in Figure 3(b), together with the resulting values for the nitrogen-to-metal ratios x . For comparison, a sample was synthesized using a poisoned target, which is the standard process utilized in industry to deposit $(\text{Ti,Al})\text{N}_x$. The oxygen content was 0.5 ± 0.1 at% for all samples. Since

oxygen can be dissolved on the nitrogen sublattice [21] the metal vacancy concentrations can be determined from the non-metal to metal ratios. These are 1.14 ± 0.04 for the sample deposited using a poisoned target and 1.08 ± 0.04 , 1.04 ± 0.04 and 0.88 ± 0.03 for the samples positioned 50, 90 and 130 mm away from the nitrogen gas inlet during combinatorial reactive magnetron sputtering, respectively. Hence, $(\text{Ti,Al})\text{N}_x$ deposited using a poisoned target and the sample deposited 50 mm away from the N_2 inlet are nitrogen overstoichiometric ($x > 1$) as predicted above based on the equilibrium between nitrogen in the gas phase and nitrogen in the growing film. The sample at 90 mm is—within the experimental error bar—stoichiometric ($x \approx 1$) and the last sample is nitrogen-deficient ($x < 1$). As discussed before off-stoichiometry is after annealing above 700°C [4,11] accommodated by metal and nitrogen vacancies [16] while for the stoichiometric sample the lower bound for the defect concentration is given by the Schottky defect concentration. Henceforth, the stoichiometries are used when referring to individual samples. The defect concentrations calculated according to Equation (2) are for $x > 1$ $c_{\text{M-vac}} = 12\% \pm 4\%$ (poisoned target) and $c_{\text{M-vac}} = 7\% \pm 4\%$, for $x < 1$ $c_{\text{N-vac}} = 12\% \pm 4\%$, respectively. The lower bound for the vacancy concentrations in $(\text{Ti,Al})\text{N}_x$ with $x \approx 1$ is the Schottky defect concentration, $c_{\text{M-vac}} = c_{\text{N-vac}} = c_{\text{Schottky}}$. The $x > 1$ sample deposited using a poisoned target therefore exhibits a similar metal vacancy concentration as the

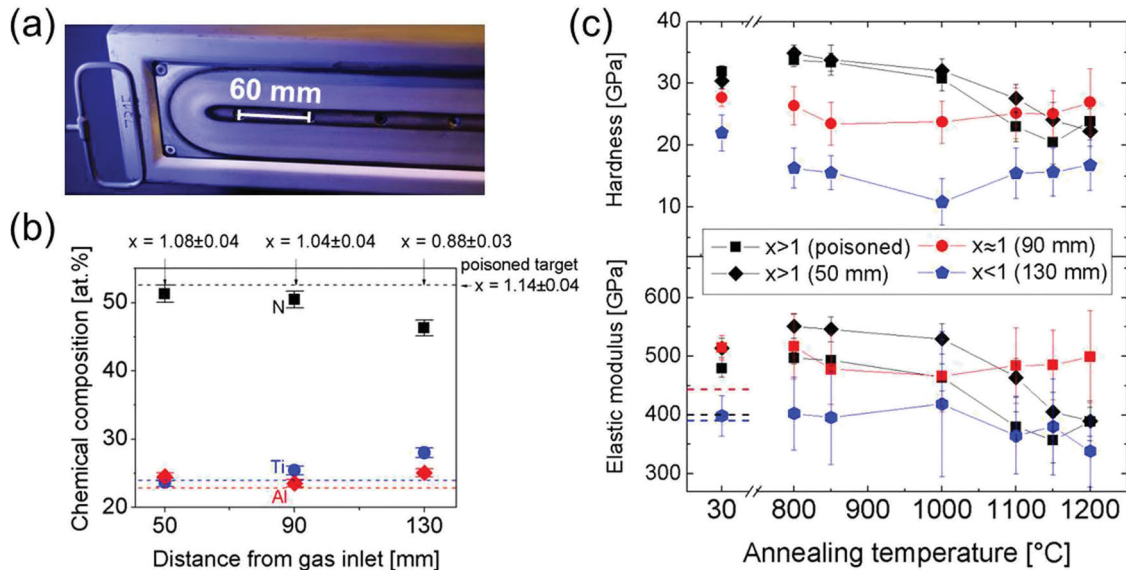


Figure 3. Deposition setup and resulting composition and mechanical properties. (a) The rectangular TiAl target and the N_2 gas inlet installed at the short side, (b) chemical composition as a function of distance from the gas inlet and for the film deposited without gas gradient using a poisoned target (dashed lines) and (c) hardness and elastic modulus determined by nanoindentation for the samples characterized by their point defect concentration as function of temperature.

Note: The dashed lines indicate calculated elastic moduli of $(\text{Ti,Al})\text{N}_x$ with $c_{\text{M-vac}} = 12\%$ (black), $c_{\text{M-vac}} = 0\%$ (red), $c_{\text{N-vac}} = 12\%$ (blue) (interpolated from data in reference [16])

one we estimated above based on the reported nitrogen loss during thermogravimetric analysis [13,14,54] and enables a direct comparison to the industrial state-of-the-art. ERDA analysis of samples annealed at 850°C showed a slight decrease in nitrogen content by 0.3 at% for $x > 1$, 0.2 at% for $x \approx 1$ and 0.9 at% for $x < 1$. Hence, only the nitrogen-understoichiometric sample has lost a considerable amount of nitrogen which might be due the fact that there is also a tendency for de-mixing on the vacancy containing nitrogen sublattice [15].

The mechanical properties are shown in Figure 3(c) as a function of annealing temperature. In the as-deposited state, the largest elastic modulus is obtained for small point defect concentrations, which is in agreement with *ab initio* calculations shown for comparison [16]. The measured elastic moduli are larger than calculated for the films with $x > 1$ and $x \approx 1$. This might be due to compressive film stresses [63–66]: Based on XSA these films exhibit compressive stresses of 3 GPa while the film with $x < 1$ exhibits a tensile stress of 1 GPa. After annealing at temperatures $< 1000^\circ\text{C}$, (Ti,Al) N_x with $x > 1$ shows a hardness increase that is attributed to be due to age hardening [4–6]. In this temperature window, it is interesting to note that (Ti,Al) N_x with $x \approx 1$ shows a slight hardness decrease indicating that there is no age hardening effect yet. However, after annealing at temperatures $> 1000^\circ\text{C}$ hardness of (Ti,Al) N_x decreases if $x > 1$ but increases slightly for $x \approx 1$, eventually leading to (Ti,Al) N_x with $x \approx 1$ exhibiting higher hardness.

To identify the relationship between vacancy concentration and thermal stability, annealing experiments followed by structural and spatially resolved chemical analysis were carried out for the stoichiometric sample as well as for under- and overstoichiometric samples. X-ray diffractograms are shown in Figure 4(a)–(c). The corresponding diffractograms for the sample deposited with a poisoned target ($x > 1$) do not show significant differences to those for the sample with $x > 1$ deposited using reactive gas gradients as can be seen in the Supplementary Figure 3. Since all films exhibited a (111) fiber texture, diffractograms are shown for the range of $35\text{--}41^\circ 2\theta$. In order to detect first precipitation of wurtzite-AlN X-ray diffractograms were obtained as a function of the sample tilt angle ψ , defined as the angle between surface normal and the diffraction plane. Hence, even fiber-textured AlN can be detected. Diffractograms were taken with constant incident angle while tilting the sample from $\psi = 0\text{--}75^\circ$ and the intensity was integrated. These diffractograms are shown in Supplementary Figure 4.

All films show a sharp peak in the as-deposited state that broadens after annealing as expected for a spinodal decomposition mechanism [4–6,9,10]. However, large differences in decomposition kinetics can be observed:

While the films with $x > 1$ are already decomposed significantly after annealing at 800°C , the stoichiometric film ($x \approx 1$) does only show very minor peak broadening starting at around 1150°C . (Ti,Al) N_x with $x < 1$ exhibits different decomposition behaviors where one strong component shows only very limited broadening (peak at 37.4°) while a very broad shoulder builds up between 38° and $40^\circ 2\theta$. After annealing at 900°C , a peak at $2\theta = 39.23^\circ$ can be observed that is indicative for the formation of TiAl_3 . The hypothetical disordered lattice of TiAl_3 is isostructural to the metal sublattice of (Ti,Al)N, that is, face-centered cubic, and hence might even form without precipitation by spinodal decomposition on the nitrogen sublattice. Spinodal decomposition for (Ti,Al) N_x with $x < 1$ has been investigated theoretically by Alling et al. [15] where for low $c_{\text{N-vac}}$ accumulation of nitrogen vacancies with Ti-rich regions is predicted. The here observed decomposition product Ti_3Al thus qualitatively agrees with that prediction, if we assume that decomposition is followed by ordering of Ti and Al on the metal sublattice. The sample with $x < 1$ is, however, not in focus of the current work and further experimental work is needed to determine the maximum allowed nitrogen vacancy concentration before thermal stability is compromised.

The lattice parameter difference between c-TiN and c-AlN leads to peak broadening during spinodal decomposition. In order to quantify the degree of spinodal decomposition, the (111) peak was fitted using two components (three for the film with $x < 1$ above 800°C) and the effective full-width at half-maximum (FWHM_{eff}) was determined by the following equation:

$$\text{FWHM}_{\text{eff}} = \sum (A_i * \text{FWHM}_i) / \sum A_i, \quad (5)$$

where A_i and FWHM_i are areas and FWHM of the different components, respectively. In Figure 4(d) FWHM_{eff} is shown as a function of temperature for (Ti,Al) N_x with varying nitrogen content, x . Open symbols are used to indicate the formation of a second phase (i.e. w-AlN or TiAl_3).

It should be noted that all films show with $0.18^\circ \pm 0.038^\circ$ similar FWHM_{eff} before annealing which can be interpreted as similar grain sizes in the as-deposited state. Therefore, it is reasonable to assume that differences in thermal stability are not due to different grain boundary densities. Furthermore, frequency distribution analysis of the elemental distributions by 3D-APT in the as-deposited state as shown in Supplementary Figures 5 and 6 do suggest that all elements are distributed randomly. Therefore, surface-initiated spinodal decomposition during growth [67–69] does not appear to occur on the length scale that can be probed by

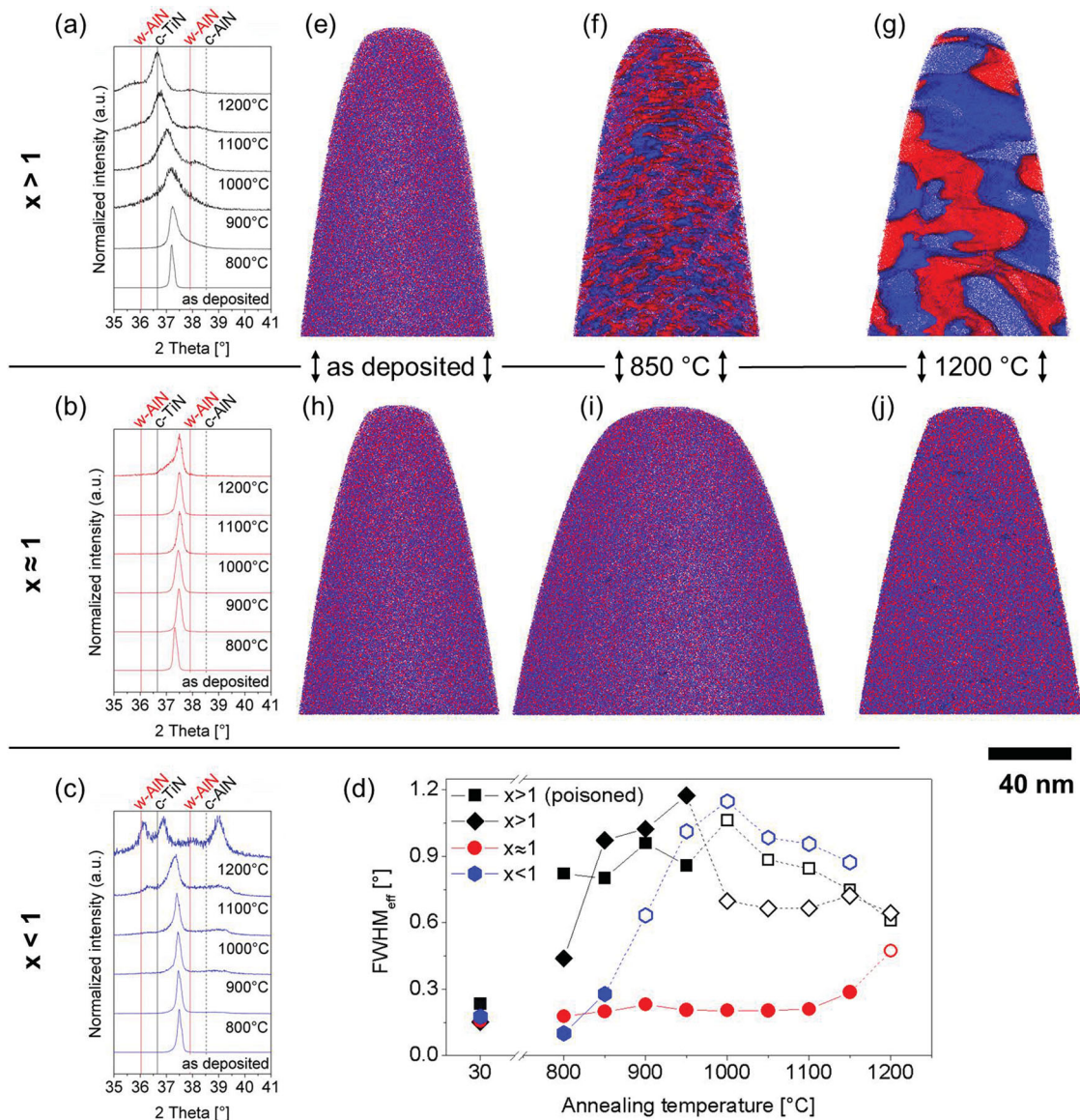


Figure 4. Structural evolution of $(\text{Ti,Al})\text{N}_x$ with different point defect concentrations after annealing. Diffraction patterns for $(\text{Ti,Al})\text{N}_x$ with $x > 1$ (a), $x \approx 1$ (b), $x < 1$ (c). (d) Effective FWHM as a measure for spinodal decomposition of the different films. Open symbols indicate the presence of a precipitated phase. Reconstructions of 3D-APT measurements of $(\text{Ti,Al})\text{N}_x$ $x > 1$ deposited using a poisoned target in the as-deposited state (e) and after annealing at 850°C (f) and 1200°C (g) and $x \approx 1$ in the as-deposited state (h) and after annealing at 850°C (i) and 1200°C (j).

Notes: Ti atoms are shown in blue, Al atoms in red. Blue surfaces are isoconcentration surfaces that indicate regions with $\text{Ti}/(\text{Ti} + \text{Al}) > 0.6$, red surfaces indicate regions with $\text{Al}/(\text{Ti} + \text{Al}) > 0.7$.

APT under the deposition conditions studied here. From the broadening it can be seen that $(\text{Ti,Al})\text{N}_x$ with $x > 1$ decomposes spinodally already at 800°C and w-AlN is formed between 950°C and 1000°C, which is in good agreement with previously published decomposition data [4,6,9–14]. The 3D-APT measurements of $(\text{Ti,Al})\text{N}_x$ with $x > 1$ show no significant composition modulations in the as-deposited state (Figure 4(e)). After annealing to 850°C spinodal decomposition into TiN- and AlN-rich regions is visible in Figure 4(f) which is in good agreement with the literature [10,70]. After annealing to 1200°C, completely phase separated TiN and AlN regions are observed, cf. Figure 4(g).

For $x < 1$ the formation of TiAl_3 starts between 900°C and 950°C, however, peak broadening is only observed at $\sim 100^\circ\text{C}$ higher temperature compared to films with $x > 1$ which could be an indication of slower spinodal decomposition.

Diffraction patterns of $(\text{Ti,Al})\text{N}_x$ with $x \approx 1$ do not show any evidence for spinodal decomposition or the formation of w-AlN at $T \leq 1100^\circ\text{C}$. Slight peak broadening is only observed at 1150°C and 1200°C. The 3D-APT measurements shown in Figure 4(h)–(j) confirm that there is no spinodal decomposition at 850°C and only minor composition modulations after annealing at 1200°C.

As can be seen in the 3D-APT reconstructions of other tips shown in Supplementary Figure 7 for the sample with $x \approx 1$, the formation of wurtzite-AlN and TiN does not take place in the whole volume but only locally, while the remainder of the volume shows only minor composition modulations. This could be due to precipitation at grain boundaries or triple junctions as has been observed during decomposition of CrN/AlN superlattices [71]. This verifies the unprecedented thermal stability increase of a metastable coating by point defect engineering. The absence of significant spinodal decomposition even after annealing at 1200°C is in excellent agreement with the theoretically predicted diffusivity change shown in Figure 2(d) between $(\text{Ti,Al})\text{N}_x$ with a constant metal vacancy concentration of 2% and stoichiometric $(\text{Ti,Al})\text{N}$ where metal vacancies are generated in Schottky defects. This corroborates our proposal that the onset temperature for spinodal decomposition is defined by the metal vacancy concentration. The low thermal stability so far limiting the application temperature of $(\text{Ti,Al})\text{N}_x$ to significantly below 1000°C is therefore only due to the fact that the synthesis conditions utilized in the last decades lead to nitrogen overstoichiometry and hence metal vacancy concentrations in the range of several percent. The 3D-APT data showing regions of TiN and AlN next to $(\text{Ti,Al})\text{N}$ for $x \approx 1$ after annealing at 1200°C indicate that thermal stability of stoichiometric $(\text{Ti,Al})\text{N}_1$ is determined by precipitation and growth of the decomposition products, rather than spinodal decomposition.

Furthermore, we have critically appraised the applicability of our research methodology for predicting stoichiometry of reactively grown thin films based on thermodynamic equilibrium between nitrogen in the gas phase and the growing film for material systems other than TiAlN. To this end we compare the reported [72] and calculated stoichiometry of $(\text{Cr,Mo})\text{N}_x$ in the Supplementary Material. Good agreement between predicted and reported transition from understoichiometric to (over)stoichiometric nitrogen content with increasing chromium content can be observed, corroborating the general applicability for other reactively deposited material systems.

Conclusions

In summary, we have shown that during reactive PVD the film composition is defined by a paraequilibrium between gas phase and the growing film. One ramification of this correlative theoretical and experimental study is the fact that $(\text{Ti,Al})\text{N}_x$ reported in the last decades contained a metal vacancy concentration of several percent. The experimentally determined

unprecedented increase in thermal stability is enabled by minimizing the population of point defects. This understanding firmly rests on high-quality RBS and ERDA quantification of the chemical composition of the samples grown by reactive gas phase combinatorics—where the metal to non-metal ratio was systematically varied—and state-of-the-art structure and spatially resolved composition analysis. Based on this understanding we have introduced a novel materials design approach using point defect engineering resulting in a 12 orders of magnitude reduced diffusivity, thus enabling the here reported unprecedented thermal stability of metastable $(\text{Ti,Al})\text{N}_x$. It is evident that the here employed combination of *ab initio* calculations to determine point defect energies with thermodynamic calculations for prediction of point defect concentrations as a function of reactive gas partial pressures can be used for point defect engineering. Thus, quantitative predictions can be made regarding what reactive gas partial pressure is needed during PVD in paraequilibrium between the gas phase and the thin film to obtain the desired stoichiometry and hence defect structure. Clearly, these results present a considerable challenge to be implemented in standard industrial coating systems utilizing threefold substrate rotation. However, hysteresis-free sputtering by HPPMS [73] as well as closed-loop control system for reactive gas flow [74] are clearly helpful for addressing this challenge. Furthermore, it is reasonable to assume that these data spawn ramifications for other reactively deposited material systems.

Disclosure statement

In accordance with Taylor & Francis policy and our ethical obligation as a researcher, we are reporting that MtB works for a company that may be affected by the research reported in the enclosed paper. We have disclosed those interests fully to Taylor & Francis, and we have in place an approved plan for managing any potential conflicts arising from that involvement.

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