

Accelerating the development of oxynitride thin films: A combinatorial investigation of the Al-Si-O-N system

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Oxynitrides are used in a variety of applications including photocatalysts, high-k dielectrics, or wear-resistant coatings and often show intriguing multifunctionality. To accelerate the cooptimization of the relevant material properties of these compositionally complex oxynitride systems, high-throughput synthesis and characterization methods are desirable. In the present work, three approaches were investigated to obtain orthogonal anion and cation gradients on the same substrate by magnetron sputtering. The different approaches included varying positions of the local reactive gas inlets and different combinations of target materials. The best performing approach was applied to screen a large two-dimensional area of the quaternary phase space within the Al-Si-O-N system. This material system is a promising candidate for transparent protective coatings with variable refractive indices. With only five depositions of combinatorial libraries, an anion composition range of 0.02–0.46 O/(N+O) and a cation composition range of 0.04–0.44 Si/(Al+Si) is covered. For lower oxygen and silicon contents, a region with hardness of up to 25 GPa is observed, where the material exhibits either wurzite AlN or a composite microstructure. By increasing the deposition temperature to 400°C, an extension of this region can be achieved. At higher oxygen and silicon contents, the structure of the samples is x-ray amorphous. In this structural region, an intimate correlation between hardness and refractive index is confirmed. The results of this study introduce a practical approach to perform high-throughput development of mixed anion materials, which is transferable to many materials systems and applications.

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I. INTRODUCTION

Oxynitrides are a versatile class of materials with a broad range of applications, including high k-dielectrics [1–3], photocatalysts [4], pigments [5,6], and phosphors [7] as well as solar-selective absorbers [8], antireflection [9] and protective coatings [10,11], and gas diffusion barriers [3,12]. This versatility is enabled by the tunability of the properties of oxynitrides via the anion composition. Properties like electrical conductivity [13], band gap [5], optical constants [8,11], and mechanical properties like hardness and elastic constants [11,13,14] or biomedical compatibility [15,16] can vary over a significant range from the oxide's to the nitride's characteristics. A prominent example is the transition from the opaque metallic TiN to transparent TiO₂ with a band gap of >3 eV [17,18].

The compositional complexity particularly in quaternary oxynitrides ABON (A,B indicating metal ions) makes their development via trial-and-error inherently time-consuming.

Combinatorial workflows using gradient deposition promise rapid materials development [19]. However, today, this type of composition screening is typically limited to gradients in cation composition, even in the case of oxynitride coatings [20–25]. The ability to perform a two-dimensional screening by simultaneously obtaining cation (A-B) and anion (O-N) gradients can accelerate the development of oxynitrides significantly. Reports about the combinatorial screening of anions are generally rare and often limited to heavier anions, e.g., Se and Te [26,27]. Only a few groups have reported on intentional gradients in either the nitrogen or the oxygen content. These were achieved in magnetron sputtering via an asymmetric N₂ gas inlet [28], varying O₂ flows with time [29], or differently oxidized precursors in molecular beam epitaxy (MBE) [30]. Gradients in the oxygen-to-nitrogen ratio, as of interest for oxynitrides, have been reported for chemical vapor deposition (CVD) [31,32] and pulsed laser deposition (PLD) [33] combinatorial depositions, while keeping the cation stoichiometry fixed. To the best of our knowledge, combinatorial gradients of the oxygen-to-nitrogen ratio in magnetron sputtering has been only reported for cosputtering of oxide and nitride compounds with different cations, which lead to overlaying cation and anion gradients [34,35], and consequently does not allow for a decoupling of the effects of cation and anion composition. Instead, it would be of high interest to investigate approaches that enable to obtain controllable O/N-gradients perpendicular to a cation gradient to

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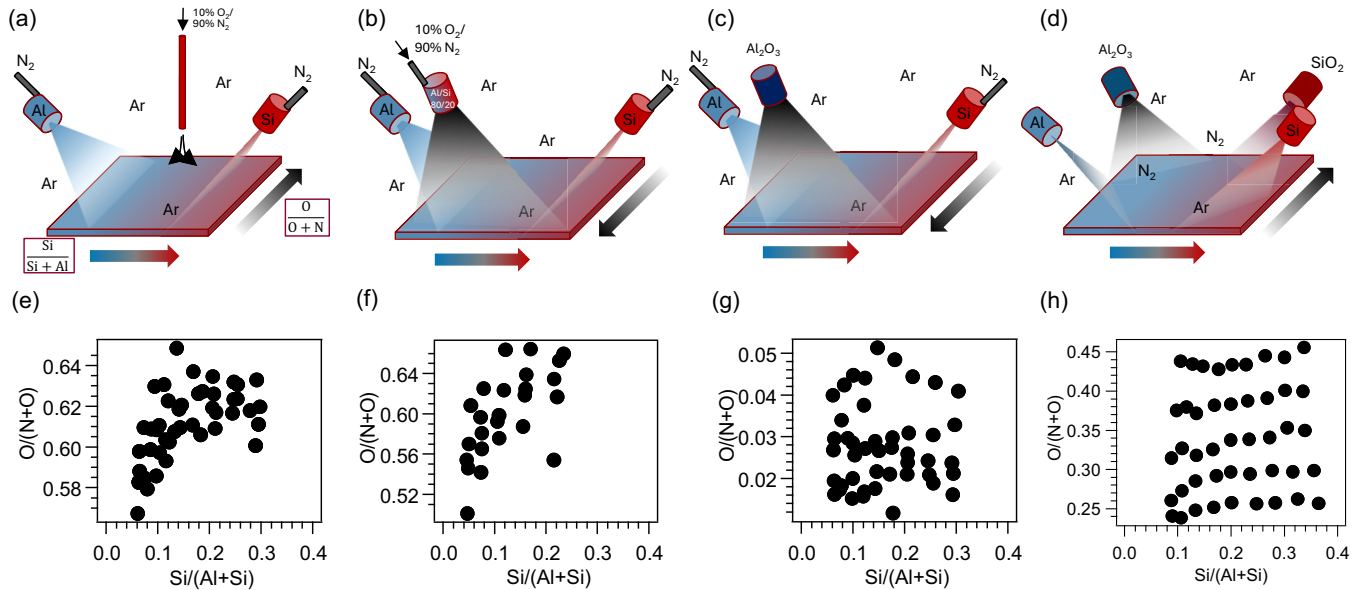


FIG. 1. Different approaches to obtain O/N gradients on combinatorial libraries perpendicular to a cation gradient: Deposition setups (a)–(d) and exemplary anion and cation ratios for a single materials library as measured by XPS for the corresponding setups (e)–(h).

analyze the dependencies on cation and anion stoichiometry independently and to maximize the area covered in quaternary oxynitride phase spaces.

For a proof of principle, the quaternary Al-Si-O-N system is a promising candidate, since the ternary systems Al-Si-N [36–39] and Al-O-N [11] are already well investigated for magnetron sputtered coatings. Moreover, this material system is promising for the application as a multifunctional protective antireflection coating, where mechanically robust, low refractive index materials are of interest. The ternary systems are reported to exhibit compositional regimes with a nanocomposite microstructure [11,38,40] with a hardness of up to 32 GPa in the Al-Si-N system [37]. Additionally, the refractive index can be tuned between 1.6 and 2.2 via the oxygen-to-nitrogen ratio in the Al-O-N system [11,41]. The current limitation in the applicability of Al-O-N for durable antireflection coatings is the reported decrease in hardness accompanying a reduction of the refractive index [11,41]. To investigate whether an independent control of hardness and refractive index is possible in the Al-Si-O-N system, a comprehensive 2D screening of the phase space would be necessary.

In this work, we compare different methods to obtain orthogonal anion and cation gradients and apply them to screen the phase space of the quaternary Al-Si-O-N system. For this purpose, we investigated three different setups to obtain O/N-gradients via reactive magnetron sputtering, including local gas inlets and varying target material combinations. We find that the combination of metallic and oxide targets sputtered in an N₂/Ar atmosphere allows for the best control in obtaining independent anion and cation gradients. Applying this approach, we screen anion compositions of 0.02–0.46 O/(N+O) and cation compositions of 0.04–0.44 Si/(Al+Si) and study the impact of anion and cation composition on hardness and refractive index. In addition, we investigate the influence of varying deposition temperatures on the optical and mechanical properties of the

coatings. We find an extension of the high hardness “composite” phase toward higher silicon and oxygen contents with increasing deposition temperature. Outside this region, our results confirm an intimate coupling between refractive index and hardness as documented in prior studies [11,41]. The results of our work introduce a practical approach to perform combinatorial screening of compositionally complex mixed-anion systems, which is broadly applicable.

II. MATERIALS AND METHODS

A. Thin film deposition

Thin film material libraries were deposited by reactive magnetron cosputtering from two to four targets in an AJA ATC-1500 sputter tool with confocal sputter-up geometry. In Fig. 1, the target configurations and locations of the reactive gas inlets for different strategies for achieving compositional gradients are depicted. A detailed description of the different approaches is provided in the Results and Discussion section. The following two-inch targets were used depending on the deposition approach: Aluminum (99.9995% purity, Kurt J. Lesker Company Ltd.) and B-doped silicon (99.999% purity, HMW Hauner GmbH & Co. KG) as well as an alloy target Al/Si 80 at.%/20 at.% (Plansee) and ceramic Al₂O₃ and SiO₂ targets (99.99% purity, Kurt J. Lesker Company Ltd.). High power impulse magnetron sputtering (HiPIMS) was applied to the metallic Al target to support densification of the coatings, while direct current magnetron sputtering (DCMS) was used for the metallic Si target. Applying this hybrid Al-HiPIMS/Si-DCMS approach, Lewin *et al.* have reported an increase in hardness compared to coatings deposited with Al-DCMS/Si-DCMS [42], which was observed in preliminary studies of our group as well. The DC power applied to the metallic Si target was 15–25 W, while the HiPIMS power of 50–100 W was applied to the Al target by a HiPSTER 1 bipolar power supply from Ionautics. Frequency (4250–7500 Hz) and pulse width (10 μs) were chosen based on previous results [43,44],

leading to peak currents of 10 ± 1 A at the beginning of the deposition, which typically dropped after several process hours to 7–8 A or in case of longer target life down to 4 A. Oxide targets were sputtered with radio-frequency magnetron sputtering (RFMS) at powers between 60 and 75 W, the Al/Si alloy target at 50 W. All magnetrons were unbalanced and—except from the first approach—open-field configurations were used. Depositions were typically performed at 5.5 ± 0.2 μ bar pressure with a gas composition of 14:6 sccm Ar:N₂ (all 99.9999% pure), while argon was supplied at the bottom of the chamber and nitrogen directly to the metallic Al and Si targets. Depending on the approach, additional O₂ or 10% O₂ in N₂ gas mixtures were used (99.999% purity). To reduce the O₂ fraction in the sputter atmosphere, gas flows of 28:12 sccm Ar:N₂ were chosen, when O₂ was used (keeping 5.5 ± 0.2 μ bar pressure). The Corning EAGLE XG substrates (2'' $\times$ 2'', 1.1 mm thick) were static and either not intentionally heated or heated to approximately 410°C. The choice of the employed substrate size was governed by the deposition rates achievable with the particular chamber geometry and the utilization of two-inch-diameter targets. The approaches may be transferable to larger substrate wafers, if larger sputter targets are employed, as commonly reported in other combinatorial studies [45]. Prior to deposition, substrates were cleaned for 5 min in acetone and ethanol in an ultrasonic bath. The substrate was sputter cleaned by applying 100 V RF bias (10–11 W) before deposition. The presputtering target cleaning was performed for 26 min at 5.5 μ bar in Ar and the target poisoning procedure was held for 4 min at 5.5 μ bar with 14:6 sccm Ar:N₂. Applying an RF bias to the substrate during deposition lead to significant Ar incorporation into the films (cf. Fig. S4 [46]), leading to partial delamination above a certain film thickness. Therefore, the presented sample libraries were deposited without the application of a substrate bias (grounded holder, floating glass substrate). To obtain sufficiently thick films for the nanoindentation measurements, the deposition times varied between 6 and 16 h. The base pressure was always below 4×10^{-8} mbar.

B. Characterization

High-throughput characterization techniques were applied after the deposition on 45 predefined sample points on each materials library: Starting with x-ray photoelectron spectroscopy (XPS) mapping, followed by x-ray diffraction (XRD), UV-Vis-NIR spectrophotometry and nanoindentation. Compositional analysis was performed by x-ray photoelectron spectroscopy on a PHI Quantera system after 10 min 2 kV Ar⁺ sputter cleaning to remove the surface oxide layer. Monochromatized Al K α_1 radiation was used for excitation, while the anode was operated at 50 W and 15 kV with a spot size of 200 μ m. A dual beam neutralizer (electrons and Ar⁺ ions) was used to mitigate charging issues. Compositions were determined after Shirley background subtraction (with an additional offset in the case of Si 2p) using the CasaXPS software. To calibrate the anion composition obtained after sputtering, heavy ion ToF-ERDA (HI-ERDA) measurements were performed with a 13 MeV iodine beam under a total scattering angle of 36° on selected samples at the Laboratory of Ion Beam Physics at ETH Zurich [47]. The calibration

curve and exemplary ERDA results are displayed in Fig. S2 [46]. The specific procedure for samples analyzed via UHV transfer between deposition chamber and XPS can be found in the Supplemental Material [46].

Structural analysis was performed by XRD on a Bruker D8 Discover equipped with a 4-circle goniometer and Cu K α source. The duration of the measurement was 14 min per sample point, i.e., 10.5 h per materials library with 45 sample points. Transmission electron microscopy (TEM) was performed using a JEM-2200FS JEOL electron microscope operated at 200 keV. The cross-sectional TEM samples were prepared by using the lift-out method in a dual-beam focused ion beam (a FEI Helios NanoLab G3 UC Dual Beam SEM/Ga⁺ FIB system). The final TEM sample thinning was done at an ion current of 24 pA at 5 kV to a thickness below 100 nm.

UV-Vis-NIR spectrophotometry measurements were executed on a home-built setup in the range of 200–1100 nm, equipped with an Ocean Optics DH-2000-BAL Deuterium-Halogen light source and two Ocean Optics HR4Pro XR-ES CCD detectors. To access the different predefined sample points, the libraries were moved through the beam path (beam size < 2 mm²) by a Thorlabs LTS300 biaxial stepper motor stage, while the optics stayed fixed. Detailed information on the setup can be found in Ref. [48]. The spectra were acquired for 3 min per sample point (10 ms integration time, 18 000 scans averaged), i.e., 2.5 h per materials library including reference samples. Refractive indices, thickness, and absorption coefficients were determined from the transmission spectra using Swanepoel's envelope method [49–51] implemented in a MATLAB script. More information on the code is provided in the Supplemental Material [46]. The determined values for the film thickness vary between 500 and 2100 nm.

Nanoindentation mapping was performed under load control using a Fischer Picodentor HM 500 equipped with a diamond Berkovich indenter. Indentation hardness and reduced Young's modulus were determined using the Oliver-Pharr method [52], fitting the unloading curve with a polynomial between 20–98% of the load. Nine load-controlled indents were executed on each sample point, 20 μ m apart, to a maximum indentation depth of 150 nm (contact depth $\approx$ 130 nm). The procedure for determining the maximum indentation depth is described in the Supplemental Material [46] (including Ref. [53]).

III. RESULTS AND DISCUSSION

A. Approaches for O/N-gradients

Figure 1 shows different approaches to control anion gradients perpendicular to a cation gradient. The basic setup consists of two metallic targets, aluminum and silicon, which were oriented opposite to each other in a confocal sputter-up geometry, while reactively sputtering in an Ar/N₂ atmosphere without substrate rotation. This produced a gradient in the cation concentration between typically $\sim$ 0.05 and 0.30 or 0.45 Si/(Al+Si) depending on the specific target powers employed. As a first approach, a local O₂ gas inlet via a nozzle was installed close to one edge of the substrate to obtain a

gradient in the O/N ratio perpendicular to the cation gradient (see Fig. 1(a) for a schematic sketch and Fig. S5(a) for a photograph [46]). N₂, however, is directed to the sputter guns. The basic idea behind this setup is that the local gas inlet would produce a variation in oxygen partial pressure across the library, while avoiding oxygen poisoning of the Al and Si targets. Consequently, arriving metal species (atoms or ions) would react at the substrate surface with varying ratios of oxygen and nitrogen species during film growth. The concept of this setup with separated gas inlets was inspired by the work of Fischer *et al.*, who aimed to stabilize the deposition process of Al-O-N [54], and Han *et al.*, who varied the N-doping in MnTe over a combinatorial library via an asymmetric gas inlet [28]. For the second approach [Fig. 1(b)], the O/N gradient was to be obtained by sputtered oxygen species from a third, oxygen-poisoned target. Therefore, O₂ containing gas was injected directly to an alloy target with Al/Si = 80/20 composition. This target composition was selected to reduce the influence on the cation gradient. For the third approach [Fig. 1(c)], an oxide target was used instead of O₂-containing gas. This can be compared to the use of differently oxidized precursors in MBE [30] or the use of oxide and nitride compound targets in PLD [33]. To reduce the effect of additional temperature gradients due to plasma heating or a gradient in Ar-bombardment across the library, the magnetic configuration requires attention. For the setups with more than two magnetrons, the open-field configuration was chosen as the most symmetrical option.

Below the schematic deposition schemes, representative anion and cation spreads measured by XPS are displayed in Figs. 1(e)–1(g). For both approaches using O₂ gas, the anion and cation gradients are not independent, as the approaches lead to anion gradients with a significant contribution in the same direction as the cation gradient. Furthermore, the obtained relative spread in the O/N ratios per library is comparably small (less than 15% per library). In both cases partial oxygen poisoning of the targets contributes to an increase in the overall oxygen content, while a different poisoning behavior of the silicon and the aluminum targets further convolutes the cation and anion gradients. This is consistent with an earlier onset of oxygen poisoning of the silicon target compared to aluminum as observed in hysteresis experiments (cf. Figs. S6a–S6c [46]). A second contributing factor could be the different affinities of Al and Si species to react with oxygen at the substrate surface. The formation enthalpies of both oxides and nitrides are collected in Table S1 [46,55]. Silicon exhibits oxide formation enthalpies which are ~3.7 times higher than those of the nitride, while this factor is only ~2.6 in the case of aluminum, which could lead to the higher O/(N+O) ratios in the silicon-rich samples.

The third approach—avoiding O₂ gas supply—exhibits independent anion and cation gradients [see Fig. 1(g)]. Sputtering from the oxide target presumably supplies a directional flux of oxygen species apparently without the limitation of a high background partial pressure of oxygen in the vacuum chamber. Although this approach results in reproducible O/N gradients, the three-magnetron setup presented has limitations when higher oxygen levels are of interest, since the only oxygen source is also an aluminum source. To mitigate this limitation, the third approach can be extended by adding a

second oxide target as depicted in Fig. 1(d), leading to orthogonal anion and cation gradients [compare Fig. 1(h)]. In addition, comparably large spreads of the O/N ratio can be achieved (more than 40% per 2''×2'' library). Successively higher oxygen contents can be conveniently obtained by increasing the power on the oxide targets and/or reducing the one of the metallic targets accordingly. Allowing for the best control to obtain independent anion and cation gradients, the third approach and its extension were applied to study the Al-Si-O-N thin film system in detail, which is presented in the following sections. Beyond this proof-of-concept within the class of oxynitrides, the presented approach may be transferred to other multianion systems including carbonitrides and oxyfluorides.

B. Two-dimensional screening of the Al-Si-O-N system

1. Structural screening

Applying the third approach and its extension introduced in the previous section, a cation range of 0.04–0.44 Si/(Al+Si) and an anion range of 0.02–0.46 O/(N+O) was screened by five depositions. The depositions were performed both at 400°C and without external heating (see Fig. S7 [46]). A first structural characterization was carried out using automated XRD mapping (see Fig. 2). Figures 2(b) and 2(c) summarize the results of the phase screening. Three different characteristic types of XRD patterns were observed: The first can be assigned to wurtzite AlN (w-AlN) featuring (002), (103), and (102) reflections [red pattern in Fig. 2(a)]. This phase has been identified at low silicon and oxygen contents [red markers in Figs. 2(b) and 2(c)]. The second type shows a shoulder or a broad peak at lower 2 θ angles adjacent to the w-AlN (002) reflection [green pattern in Fig. 2(a)]. Simultaneously, the w-AlN reflection intensities decrease with increasing Si/(Al+Si) and O/(N+O) ratios. The broad hump has been attributed in the literature to lattice plane dilatation at grain boundaries or a partially ordered grain boundary phase [38]. A comparison with diffraction patterns from the ICSD database reveals that α -Si₃N₄ [57], α -Al₂O₃ [58], SiAl₄O₂N₄ [59], or mullite Al_{6(1-z)}Si_{6z}O_{9+3z} [60] could be possible candidates for the latter, exhibiting reflections in the respective region. Therefore, this phase type will be referred to as the “composite” phase region in the following and is found at intermediate Si and O contents. The third type represents peak-free patterns indicating an x-ray amorphous microstructure [purple pattern in Fig. 2(a)] and occurs at even higher oxygen and silicon concentrations. Two main observations can be made based on the cation-anion phase diagrams in Figs. 2(b) and 2(c): First, there is an apparent linear relationship between the Si/(Al+Si) and O/(N+O) fractions on the boundaries separating the three phases. Second, a slight expansion of the “w-AlN”-type region and a significant expansion of the “composite” region along the Si/(Si+Al) and O/(N+O) axes could be achieved by increasing the deposition temperature.

To assess the microstructural features of the different phase regions in more detail, cross-sectional TEM micrographs and selected area electron diffraction (SAED) pattern were obtained for three samples with low O/(N+O) ratio (0.05 ± 0.01) and 400°C deposition temperature. Figure 3(a) shows a bright-field TEM (BF-TEM) cross-sectional image

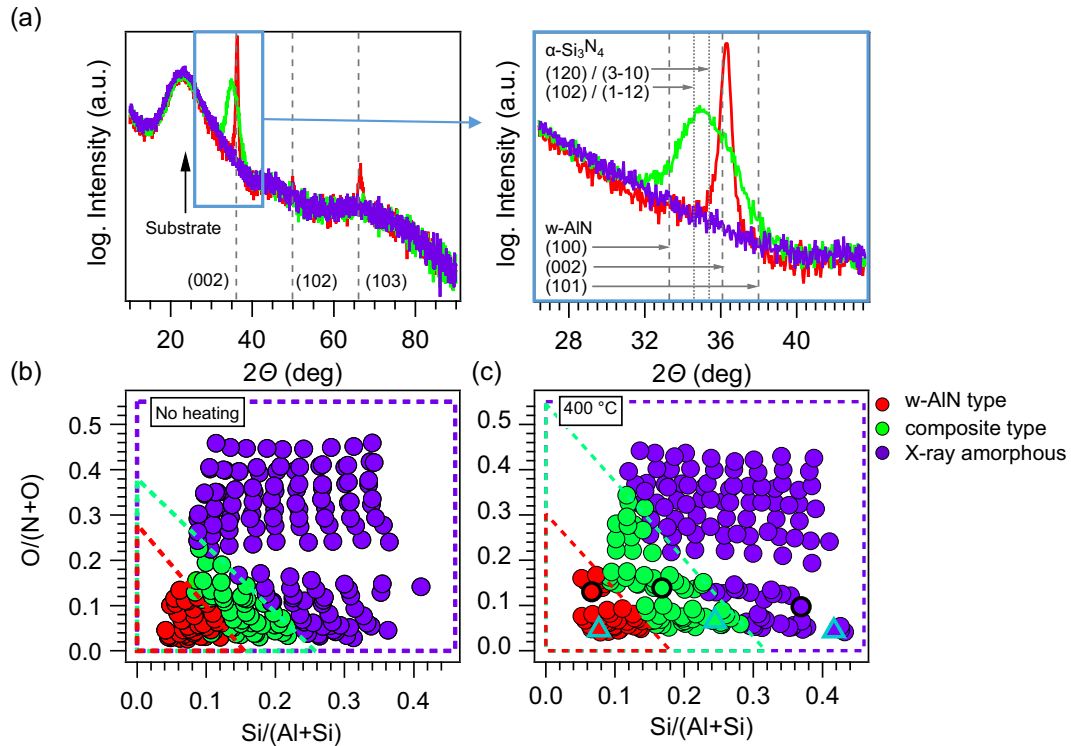


FIG. 2. Structural analysis based on automated XRD mapping: (a) Representative diffraction patterns for the three observed structural types based on wurtzite-AlN (red), a composite structure (green) and x-ray amorphous samples (violet); cation-anion phase diagram for samples deposited (b) without external heating and (c) at 400°C. The highlighted samples are those presented in panel (a) (○) and those investigated by TEM (Δ). A pattern was classified as composite type, if a second pseudo-Voigt peak is required to obtain a decent fit of the (002) reflection, and as amorphous type, if the pattern coincides with the one of the bare glass substrate. Indicated reflections are based on powder diffraction of wurtzite-AlN reported by Schulz and Thiemann [56] and α -Si₃N₄ by Yang *et al.* [57].

of the sample with $\text{Si}/(\text{Al}+\text{Si}) = 0.08$ that belongs to the “w-AlN”-type region. The film exhibits a dense microstructure composed of w-AlN columnar grains. The columnar grains are tilted by about $+10^\circ$ with respect to the substrate normal because the substrate was not rotated using a confocal sputter geometry. This phenomenon is known as the tangent rule and occurs due to shadowing and slow (surface) diffusion at low substrate temperatures [61,62]. The corresponding SAED pattern [Fig. 3(a)] reveals a series of diffraction rings associated with w-AlN implying a polycrystalline microstructure. Importantly, the {002} reflections have the highest intensity with relatively narrow angular distribution representing an arc-like diffraction intensity. The {002} reflections of the highest intensity are inclined from the film growth direction implying an abnormal (002) texture.

Figure 3(b) shows a cross-sectional BF-TEM image of a sample belonging to the “composite”-type region with $\text{Si}/(\text{Al}+\text{Si}) = 0.24$. This sample exhibits the highest intensity of the broad hump observed in the XRD pattern considering the same oxygen content [Fig. 2(a)]. The image reveals less clear features of columnar microstructure. Similar to the “w-AlN” structural type, these columns appear to be inclined due to the oblique deposition angle. The contrast modulation along and across the column boundaries suggests differences in crystallographic orientation or slight structural disorder considering the homogeneous phase composition (see EDS mapping and STEM in Fig. S9 [46]). This growth morphology is typical for interrupted columnar growth and repeated

nucleation leading to grain refinement. Corresponding SAED pattern reveals broadened diffraction rings with arc-like features, all typical for grain refinement and/or strained grains. Moreover, additional signals from α -Si₃N₄ (trigonal crystal structure, P31c space group) are present on the SAED pattern. Therefore, the broad peak in the respective XRD pattern of the “composite”-type regions presumably represents a convolution of α -Si₃N₄ (120) and (102) as well as w-AlN (002) reflections.

In Fig. 3(c), a BF-TEM cross-sectional image of the sample with $\text{Si}/(\text{Al}+\text{Si}) = 0.42$, which belongs to the “x-ray amorphous” region, is displayed showing a featureless microstructure. The corresponding SAED patterns exhibit broad diffraction rings typical for amorphous materials.

A high-resolution TEM (HRTEM) analysis of the sample with $\text{Si}/(\text{Al}+\text{Si}) = 0.08$ [Fig. 3(a)] reveals coherent lattice fringes along the [002] direction and even contrast within the grain interior. The lattice fringes are inclined by approximately 80° from the grain growth direction. This finding stands in contrast to literature reports on the ternary subsystems [11,37], as well as on pure AlN [43], in which the majority of the w-AlN (002) planes are oriented along the grain growth direction. The potential origin of this phenomenon is currently the subject of further investigation. The increase of Si content in the sample with $\text{Si}/(\text{Al}+\text{Si}) = 0.24$ causes local disruption of lattice fringes and dark contrast regions on HRTEM image [Fig. 3(b)]. The corresponding FFT pattern contains arc-shaped (002) AlN reflections caused by

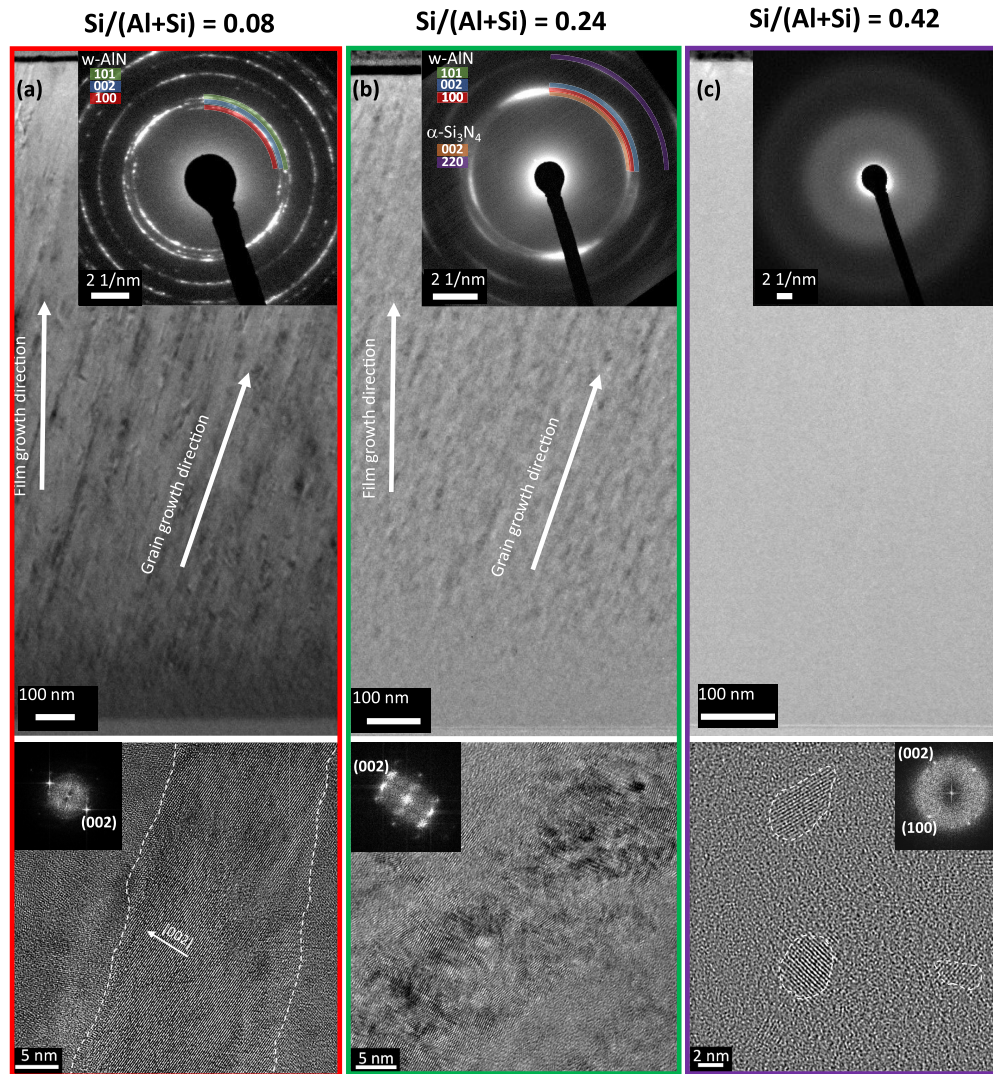


FIG. 3. Cross-sectional low-magnification (top) and high-resolution (bottom) BF-TEM images from the sample (a) with $\text{Si}/(\text{Al}+\text{Si}) = 0.08$, (b) $\text{Si}/(\text{Al}+\text{Si}) = 0.24$, and (c) $\text{Si}/(\text{Al}+\text{Si}) = 0.42$ and $\text{O}/(\text{N}+\text{O}) = 0.05 \pm 0.01$ grown at 400°C [see Δ in Fig. 2(c)]. The insets represent corresponding SAED patterns (top) and fast-Fourier transform (FFT) patterns (bottom).

small misorientations and/or overlapping between nano-scale grains in the selected area. The disruption of local epitaxial growth on individual w-AlN-based columns is a consequence of repeated nucleation during growth caused by the increase of Si content. The formation of $\alpha\text{-Si}_3\text{N}_4$ increases the nucleation rate promoting re-nucleation of w-AlN-based domains and their refinement down to a sub-nanocrystalline state. The nanocrystalline domains of $\alpha\text{-Si}_3\text{N}_4$ are observed on HRTEM images along the zone axis close to $[321]$ (Fig. S8 [46]). A scanning TEM (STEM) analysis of this sample reveals bright and dark contrast areas on both bright- and dark-field STEM images (Figs. S9(a), S9(b), and S9(c) [46]). However, EDS elemental mapping (Figs. S9(d) and S9(e) [46]) does not show any distinct contrast. This suggests that both phases w-AlN and $\alpha\text{-Si}_3\text{N}_4$ have very similar composition. Since there is no contrast on EDS mapping, the contrast on STEM images can be of crystallographic origin caused by overlapping or slightly misoriented grains.

Upon further increase of the Si content up to $\text{Si}/(\text{Al}+\text{Si}) = 0.42$, the presence of small (2–5 nm diameter),

randomly oriented equiaxed w-AlN grains surrounded by an amorphous matrix can be observed on the HRTEM images [Fig. 3(c)]. Due to their small size, these grains were not detected by the XRD mapping. Similar findings have been reported by Pélissier *et al.* [37], Musil *et al.* [40], and Fischer *et al.* [11].

A similar microstructural evolution has been reported in the literature for the ternary systems Al-Si-N and Al-O-N. Four regions are differentiated [11,37,38]: A solid solution of Si or O in w-AlN is followed by a nanocomposite of w-AlN grains surrounded by a thin grain boundary phase. A further increase in Si or O content leads to a thickening of the grain boundary phase, finally ending in an amorphous phase. In the present study, the observed shift of the (002) peak position in the XRD patterns indicate that the Si solubility limit is located within the “w-AlN”-type region and depends on the substrate temperature and O content. The solubility limit of Si strongly depends on the O content for the samples grown without intentional substrate heating. At high O contents, the Si solubility is around $\text{Si}/(\text{Al}+\text{Si}) = 0.07$, while at low O content the

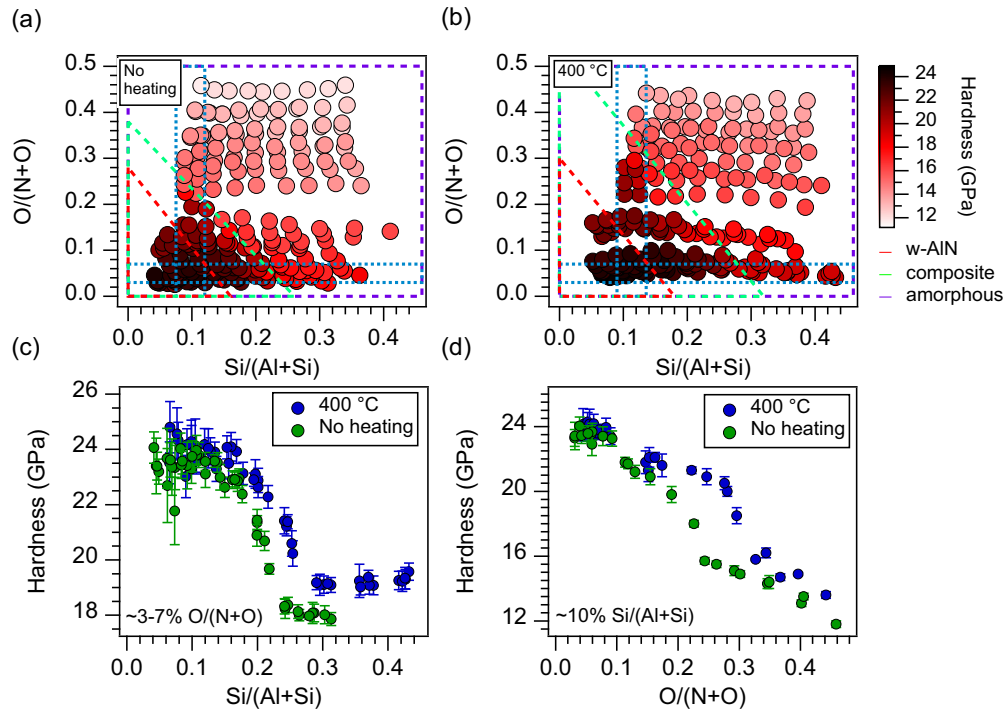


FIG. 4. Nanoindentation mapping results for Al-Si-O-N thin film libraries: Hardness as a function of the anion and cation composition for libraries deposited (a) without external heating and (b) at 400°C. The dashed lines indicate the presence of the structural types observed in Fig. 2. Cross sections of hardness versus (c) cation composition at low oxygen content and versus (d) anion composition at low silicon content. Markers denote the mean; error bars indicate the standard deviation over nine indents.

solubility extends up to $\text{Si}/(\text{Al}+\text{Si}) = 0.13$. In contrast, at 400°C deposition temperature, the Si solubility does not depend on O content and is around $\text{Si}/(\text{Al}+\text{Si}) = 0.08$ (cf. Fig. S10 [46]). Therefore, the “w-AlN”-type region (red) likely encompasses both a solid solution and a first nanocomposite regime with a thin grain boundary phase not detectable by the XRD mapping procedure and not covered by our TEM investigation. Within the subsequent “composite” phase (green), the volume fraction of the grain boundary phase increases leading to the formation of $\alpha\text{-Si}_3\text{N}_4$ and potentially oxide compounds for higher O contents, while the volume fraction of w-AlN based grains decreases. Continuous increase of Si and O content leads to the reduction of the grain size and their amount to a level not detectable by XRD but observable in the high resolution TEM images (purple) [see Fig. 3(c)]. Increasing the substrate temperature may promote the crystallization of w-AlN grains and in particular the nucleation of the grain boundary phase resulting in the observed significant extension of the composite region at 400°C.

2. Functional property screening

The mechanical properties of the Al-Si-O-N thin film libraries were screened using automated nanoindentation mapping. In Fig. 4, the resulting hardness values are displayed as a function of the anion and cation composition. A clear correlation with the microstructural evolution discussed in the previous section is evident. A high hardness plateau of 23–25 GPa is present in the region with “w-AlN”-type. Within the “composite” region, the hardness decays with increasing silicon and oxygen content, starting slowly followed by a steep drop close to the transition to the “x-ray

amorphous” region. While both solid solution and grain boundary hardening mechanisms presumably contribute to the hardness of the high hardness plateau, the steep drop may be related to the reduction in grain size as observed in the TEM cross-section for $\text{Si}/(\text{Al}+\text{Si}) = 0.24$ [cf. Fig. 3(b)], which may be beyond the optimal “strongest size,” after which the deformation behavior is dominated by grain-boundary-mediated mechanisms (e.g., sliding, diffusion) [63,64]. Additionally, this prominent decrease in hardness exceeding a certain silicon content has been attributed in related nanocomposite systems to the increased volume fraction of a soft amorphous SiN_x phase [65,66]. Due to the extension of the crystalline region at elevated temperatures, this decrease in hardness is shifted toward higher Si and O contents for 400°C deposition temperature. In the “x-ray amorphous” region, a second plateau is present with hardness values of 18.1 ± 0.2 GPa (no heating) or 19.3 ± 0.3 GPa (400°C) for samples with low oxygen contents of 0.03–0.07 O/(N+O) [see Fig. 4(c)]. This observation could be related to the presence of nanocrystals in the amorphous matrix as identified in the TEM micrographs [cf. Fig. 3(c)]. Their growth could be favored by faster diffusion processes at higher deposition temperatures. In addition to the observed hardness drop associated with the different microstructure types, an almost linear decrease in hardness is observed with increasing oxygen contents as visualized in Fig. 4(d). We hypothesize that a higher degree of ionicity of Al-O bonds compared to Al-N bonds contributes to this effect, resulting in lower elastic moduli and lower hardness [67].

The measured hardness values in the “w-AlN”-type and “x-ray amorphous” regions are in good agreement with those reported by Fischer *et al.* [11] and Lewin *et al.* [42].

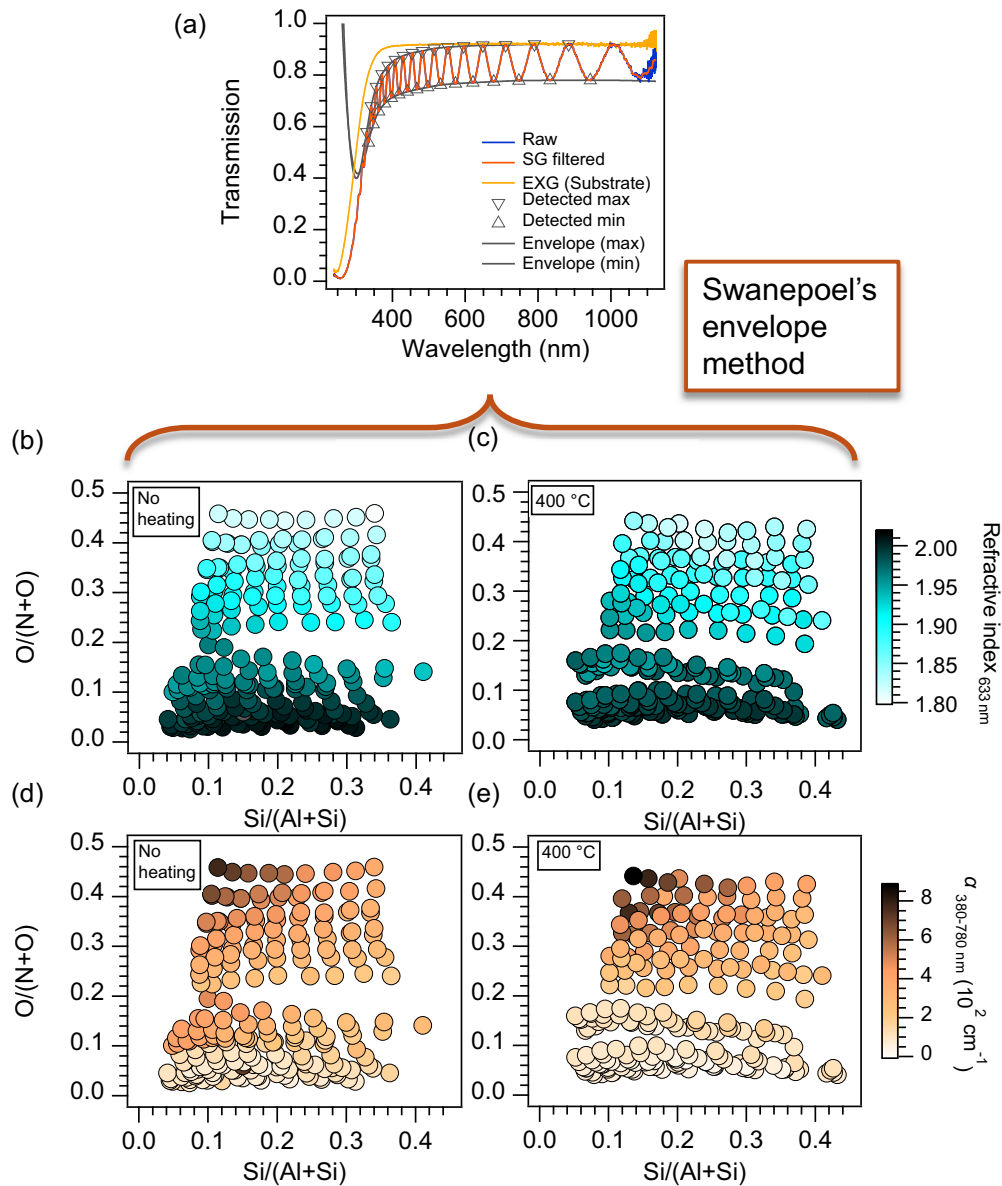


FIG. 5. Optical property screening for Al-Si-O-N thin film libraries based on UV-Vis transmission data and Swanepoel's envelope method: (a) Typical transmission spectrum of the sample on the EXG substrate, the substrate as well as determined features necessary for the Swanepoel analysis. Refractive index at 633 nm (b), (c) and the mean absorption coefficient between 380 and 780 nm (d), (e) as a function of anion and cation composition derived via the Swanepoel method.

Contrary to findings for other nanocomposite systems, the present material screening does not reveal a substantial increase in hardness for intermediate Si contents, where the hardening due to the “strongest size” effect could have been expected due to a nanocomposite microstructure [67–69]. On the one hand, the applied process conditions and oxygen contents > 0.01 O/(N+O) may not result in the required microstructure of 10–15 nm sized w-AlN grains embedded in a monolayer thick SiN_x grain boundary phase with a sharp interface [70–72]. On the other hand, theoretical calculations by Sheng *et al.* suggest that spinodal decomposition is improbable in the Al-Si-N system, which hinders the formation of the microstructure required for a strong hardness enhancement, and could therefore represent a general limitation in this material system [73].

To assess the optical constants in a quick and automated manner, the Swanepoel method was implemented to extract the desired quantities from UV-Vis-NIR transmission spectra. The required features determined from the interference extrema of the transmission spectra are visualized in Fig. 5(a), while the detailed procedure is described in the Supplemental Material [46]. In contrast to the hardness, a correlation between the refractive index at 633 nm and the determined structure types is barely perceptible [see Figs. 5(b) and 5(c)]. Therefore, the deposition temperature has no significant influence on the results as well. Instead, the refractive index decreases approximately linearly with increasing O/(N+O) ratio from 2.02 to 1.80 as expected from literature reports [11,41,74,75]. According to Shannon and Fischer, the dynamic polarizability of the fourfold coordinated Al³⁺ cation

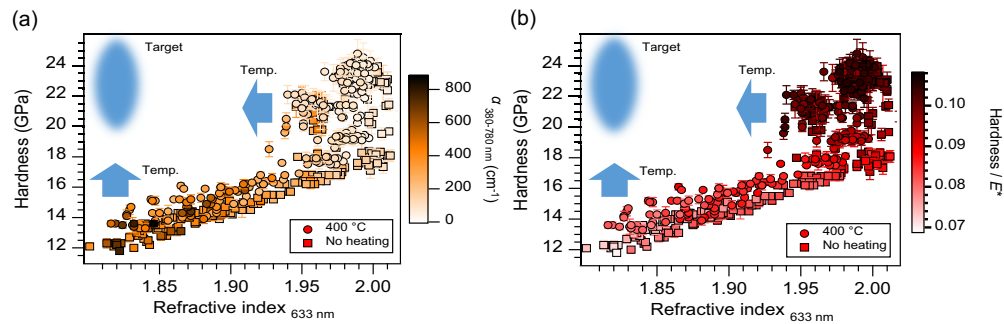


FIG. 6. Hardness (H) plotted against refractive index (n) with different marker color codes for Al-Si-O-N thin film libraries: (a) mean absorption coefficient between 380 and 780 nm and (b) hardness/effective Young's modulus (H/E^*) ratio. Blue spots indicate the desired target area.

($0.533 \text{ \AA}^3$) exceeds that of Si^{4+} ($0.284 \text{ \AA}^3$) [76]. Therefore, a decrease in the refractive index is expected with increasing silicon cation substitution, which can be inferred from the present data for higher oxygen contents. However, the extent of this variation is significantly lower than that due to the $\text{O}/(\text{N}+\text{O})$ ratio. Indeed, the anion polarizability is significantly higher and has a stronger influence on the refractive index. As presented in the Supplemental Material [46], the application of the Anderson-Eggleton equation as given by Shannon and Fischer [76] enables the calculation of the nitrogen polarizability in the visible range based on the refractive index and the sample composition. Values between 2.4 and $2.8 \text{ \AA}^3$ are estimated, while decreasing polarizabilities are found for increasing oxygen contents, particularly pronounced in the “x-ray amorphous” region (cf. Fig. S11 [46]). This observation may be attributed to a reduced charge density around the nitrogen ions with more electronegative oxygen ions in close proximity. To obtain values with reduced scatter that could serve for predictive purposes, the implementation of a more sophisticated model—considering, for example, a molar volume dependence or a varying degree of covalency—may be required.

All deposited thin films were transparent. Considering the mean absorption coefficient in the visible region, the deposition temperature exhibits only a small influence, while a significant increase is observed at higher oxygen contents (as reported in literature [75]), especially for Al-rich samples. The highest contribution to the absorption originates from wavelength range $< 500 \text{ nm}$, as visualized by the maps of the absorption coefficient at different wavelengths in Fig. S12 [46]. Placing the libraries in front of a white background therefore allows the observation of a slight yellowish appearance for Al- and O-rich regions (see Fig. S13 [46]). The increased absorption could arise due to scattering at inclusions or precipitates [77]. Their coherent size may be below the inherent detection limit of the XRD mapping.

As mentioned above, hard, resilient coatings with tunable refractive indices are of particular importance in the field of protective antireflective coatings. To visualize the results of the cooptimization, hardness H is plotted against the refractive index in Fig. 6. There is a general linear trend between hardness and refractive index, particularly for low refractive indices where exclusively the “x-ray amorphous” regime prevails. The independent tunability of hardness and refractive

index is limited to a refractive index range between 1.94 and 2.02 within the screened compositional space of the “w-AlN”-type and the “composite” microstructure. When the deposition temperature is increased to 400°C , the hardness in the “x-ray amorphous” region is raised by approximately 1 GPa for the same refractive indices. In addition, the variable hardness range is extended toward slightly lower refractive indices. Considering the extent of the observed hardness increase, the likelihood of achieving combinations of properties in the target area (blue spots in Fig. 6) appears low, even with a possible further increase in deposition temperature.

Another potential route to extend the “composite” regime toward higher oxygen contents is the reduction of the silicon content, as illustrated by Fig. 2. This could enable increased hardness also for lower refractive indices than 1.94. Nonetheless, a linear decrease with the refractive index is evident for the high hardness limit as well, representing an additional impediment to accessing the target area of $>20 \text{ GPa}$.

To assess the origin of the apparent linear correlation between hardness and refractive index, possible common descriptors are required. One possible descriptor could be a measure for the degree of bond ionicity or covalency. As described in the Supplemental Material [46] (including Refs. [78,79]), the XPS binding energy difference between anion and cations can represent a measure for bond covalency. Following these considerations, Fig. S14 illustrates that refractive index, hardness and the effective Young's modulus correlate only partially to the material's covalency. A more comprehensive discussion can be found in the Supplemental Material [46].

In addition to high hardness and a suitable refractive index, a high level of transparency is desirable for the application as an antireflective coating. Figure 6(a) depicts the mean absorption coefficient in the visible spectrum as a color code showing low values of $\leq 10^2 \text{ cm}^{-1}$ for samples with the highest refractive indices and hardness. In the context of antireflection coatings on flexible substrates, the coating must demonstrate resistance to cracking during bending additionally. Musil *et al.* have found that the ratio between hardness and effective Young's modulus (H/E^*) can serve as an estimate for the resistance to cracking due to substrate bending. In their studies, no cracking was observed for coating materials with $H/E^* \geq 0.1$ [80]. As visualized in Fig. 6(b), most of the Al-Si-O-N samples of the “w-AlN”-type and “composite”-

type region fulfil this criterion. The highest values of $H/E^* \geq 0.105$ are present in high hardness and high refractive index samples with “composite”-type microstructure.

IV. CONCLUSIONS

In this study we performed a high-throughput combinatorial investigation of Al-Si-O-N thin films, exploring both cation and anion composition variations. Among all tested approaches, we determined that the combination of metallic (Al, Si) and oxide (SiO_2 and Al_2O_3) targets allowed us to achieve distinct orthogonal cation and anion gradients and a decent spread in the oxygen/nitrogen ratio across the material library. This approach enabled the screening of a compositional space of approximately 0.40 in the Si/(Al+Si) ratio and 0.45 in the O/(N+O) ratio synthesizing only five thin film libraries. This time-efficient screening allows for an additional investigation of the influence of process parameters—in this study the deposition temperature—on material properties of interest. We determined three composition-dependent types of microstructures: a “wurtzite-AlN”-based microstructure for low silicon and oxygen contents, followed by a “composite” microstructure and an x-ray amorphous microstructure for higher silicon and oxygen contents. The measured hardness followed these structural zones, starting with a high hardness plateau of 23–25 GPa for the “wurtzite AlN”-type phase, undergoing a drop at the transition between the “composite” and the “x-ray amorphous” phase, and reaching another hardness plateau of 18–19 GPa at low oxygen contents. An increase in the oxygen content superposes a further linear decrease in hardness down to 11.5 GPa. The plateau of high hardness could be extended by increasing the deposition temperature to 400°C with 0.05 Si/(Al+Si) and 0.08 O/(N+O). In contrast, in agreement with the previous reports, the refractive index is mainly influenced by the oxygen/nitrogen ratio and to a

lesser extent by the cation ratio, resulting in a span between 1.80 and 2.02 within the screened composition space. Our results illustrate the linear correlation between refractive index and hardness, particularly within the “x-ray amorphous” region. The higher hardness phase, which allows this linear relationship to be overcome, is strongly constrained in the compositional space. Consequently, the ability to tune the refractive index yet keeping high hardness values is also significantly limited in this material system.

With this proof-of-principle, we hope to encourage other researchers to adopt the herein presented methodology for orthogonal anion and cation gradients to other compositionally complex systems, including carbonitrides and oxyfluorides, potentially accelerating development in many other application fields.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [81]; embargo periods may apply.

- [1] M. Koyama *et al.*, Effects of nitrogen in HfSiON gate dielectric on the electrical and thermal characteristics, in *Technical Digest—International Electron Devices Meeting (IEDM)* (IEEE, Piscataway, NJ, 2002), pp. 849–852.
- [2] L.-P. Feng and Z.-T. Liu, HfSiON films deposited by radio frequency reactive sputtering, in *Metallic Oxynitride Thin Films by Reactive Sputtering and Related Deposition Methods: Process, Properties and Applications*, edited by F. Vaz, N. Martin, and M. Fenker (Bentham Science Publishers, Sharjah, United Arab Emirates, 2013), pp. 230–253.
- [3] Y.-H. Wu and J.-H. Huang, Application of oxynitrides for microelectronic device and gas barriers, in *Metallic Oxynitride Thin Films by Reactive Sputtering and Related Deposition Methods: Process, Properties and Applications*, edited by F. Vaz, N. Martin, and M. Fenker (Bentham Science Publisher, Sharjah, United Arab Emirates, 2013), pp. 285–339.
- [4] G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, An oxynitride, TaON, as an efficient water oxidation photocatalyst under visible light irradiation ($\lambda \leq 500$ nm), *Chem. Commun.* **2**, 1698 (2002).
- [5] R. J. Xie and H. T. Hintzen, Optical properties of (oxy)nitride materials: A review, *J. Am. Ceram. Soc.* **96**, 665 (2013).
- [6] Y.-I. Kim, Syntheses, crystal structures, and dielectric property of oxynitride perovskites, Ph.D. thesis, Ohio State University, 2005.
- [7] S. Yamada, H. Emoto, M. Ibukiyama, and N. Hirotsaki, Properties of SiAlON powder phosphors for white LEDs, *J. Eur. Ceram. Soc.* **32**, 1355 (2012).
- [8] L. Rebouta, A. Sousa, M. Andritschky, F. Cerqueira, C. J. Tavares, P. Santilli, and K. Pischow, Solar selective absorbing coatings based on AlSiN/AlSiON/AlSiO_y layers, *Appl. Surf. Sci.* **356**, 203 (2015).
- [9] Y. Wang, X. Cheng, Z. Lin, C. Zhang, and F. Zhang, Optimization of PECVD silicon oxynitride films for anti-reflection coating, *Vacuum* **72**, 345 (2003).
- [10] M. Urgan, V. Ezirmik, E. Senel, Z. Kahraman, and K. Kazmanli, The effect of oxygen content on the temperature dependent tribological behavior of Cr-O-N coatings, *Surf. Coatings Technol.* **203**, 2272 (2009).
- [11] M. Fischer, M. Trant, K. Thorwarth, R. Crockett, J. Patscheider, and H. J. Hug, Understanding the microstructural evolution and mechanical properties of transparent Al-O-N and Al-Si-O-N films, *Sci. Technol. Adv. Mater.* **20**, 1031 (2019).
- [12] M. C. Lin, L. S. Chang, and H. C. Lin, Gas barrier properties of titanium oxynitride films deposited on polyethylene tereph-

- thalate substrates by reactive magnetron sputtering, *Appl. Surf. Sci.* **254**, 3509 (2008).
- [13] P. Carvalho, L. Cunha, N. P. Barradas, E. Alves, J. P. Espinos, and F. Vaz, Tuneable properties of zirconium oxynitride thin films, in *Metallic Oxynitride Thin Films by Reactive Sputtering and Related Deposition Methods*, edited by F. Vaz, N. Martin, and M. Fenker (Bentham Science Publishers, Sharjah, United Arab Emirates, 2013), pp. 64–112.
 - [14] J. Vetter, Oxynitrides and oxides deposited by cathodic vacuum arc, in *Metallic Oxynitride Thin Films by Reactive Sputtering and Related Deposition Methods: Process, Properties and Applications*, edited by F. Vaz, N. Martin, and M. Fenker (Bentham Science Publishers, Sharjah, United Arab Emirates, 2013), pp. 265–284.
 - [15] G. J. Wan, N. Huang, S. C. H. Kwok, Z. Y. Shao, A. S. Zhao, P. Yang, and P. K. Chu, Si-N-O films synthesized by plasma immersion ion implantation and deposition (PIII&D) for blood-contacting biomedical applications, *IEEE Trans. Plasma Sci.* **34**, 1160 (2006).
 - [16] M. Fenker, Properties of oxynitride thin films for biomedical applications, in *Metallic Oxynitride Thin Films by Reactive Sputtering and Related Deposition Methods: Process, Properties and Applications*, edited by F. Vaz, N. Martin, and M. Fenker (Bentham Science Publishers, Sharjah, United Arab Emirates, 2013), pp. 254–264.
 - [17] D. Heřman, J. Šícha, and J. Musil, Magnetron sputtering of TiO_xN_y films, *Vacuum* **81**, 285 (2006).
 - [18] H. Akazawa, Transparent conductive properties of TiON thin films, *J. Vac. Sci. Technol. A* **40**, 013407 (2022).
 - [19] K. Alberi *et al.*, The 2019 materials by design roadmap, *J. Phys. D: Appl. Phys.* **52**, 013001 (2019).
 - [20] M. Stueber, D. Diechle, H. Leiste, and S. Ulrich, Synthesis of Al-Cr-O-N thin films in corundum and f.c.c. structure by reactive r.f. magnetron sputtering, *Thin. Solid. Films* **519**, 4025 (2011).
 - [21] D. Diechle, M. Stueber, H. Leiste, and S. Ulrich, Combinatorial approach to the growth of $\alpha - (\text{Al}_{1-x}, \text{Cr}_x)_{2+\delta}(\text{O}_{1-y}, \text{N}_y)_3$ solid solution strengthened thin films by reactive r.f. magnetron sputtering, *Surf. Coatings Technol.* **206**, 1545 (2011).
 - [22] S. Spitz, M. Stueber, H. Leiste, S. Ulrich, and H. J. Seifert, Phase formation and microstructure evolution of reactively r.f. magnetron sputtered Cr-Zr oxynitride thin films, *Surf. Coatings Technol.* **237**, 149 (2013).
 - [23] C. L. L. Melamed, M. B. B. Tellekamp, J. S. S. Mangum, J. D. D. Perkins, P. Dippe, E. S. S. Toberer, and A. C. Tamboli, Blue-green emission from epitaxial yet cation-disordered $\text{ZnGeN}_{2-x}\text{O}_x$, *Phys. Rev. Mater.* **3**, 051602 (2019).
 - [24] S. K. Suram, S. W. Fackler, L. Zhou, A. T. N'Diaye, W. S. Drisdell, J. Yano, and J. M. Gregoire, Combinatorial discovery of lanthanum–tantalum oxynitride solar light absorbers with dilute nitrogen for solar fuel applications, *ACS Comb. Sci.* **20**, 26 (2018).
 - [25] K. R. Talley, J. Mangum, C. L. Perkins, R. Woods-Robinson, A. Mehta, B. P. Gorman, G. L. Brennecke, and A. Zakutayev, Synthesis of lanthanum tungsten oxynitride perovskite thin films, *Adv. Electron. Mater.* **5**, 1900214 (2019).
 - [26] S. Siol, A. Holder, B. R. B. R. Ortiz, P. A. P. A. Parilla, E. Toberer, S. Lany, and A. Zakutayev, Solubility limits in quaternary SnTe-based alloys, *RSC Adv.* **7**, 24747 (2017).
 - [27] S. Siol *et al.*, Negative-pressure polymorphs made by heterostructural alloying, *Sci. Adv.* **4**, eaaq1442 (2018).
 - [28] Y. Han, B. Matthews, D. Roberts, K. R. Talley, S. R. Bauers, C. Perkins, Q. Zhang, and A. Zakutayev, Combinatorial nitrogen gradients in sputtered thin films, *ACS Comb. Sci.* **20**, 436 (2018).
 - [29] J. Park, S. H. Shin, J. S. Bae, X. Zhang, I. Takeuchi, and S. Lee, Combinatorial synthesis of non-stoichiometric SiO_x thin films via high-throughput reactive sputtering, *J. Appl. Phys.* **129**, 155309 (2021).
 - [30] H. T. Zhang, L. Zhang, D. Mukherjee, Y. X. Zheng, R. C. Haislmaier, N. Alem, and R. Engel-Herbert, Wafer-scale growth of VO_2 thin films using a combinatorial approach, *Nat. Commun.* **6**, 8475 (2015).
 - [31] G. Hyett and I. P. Parkin, A combinatorial approach to phase synthesis and characterisation in atmospheric pressure chemical vapour deposition, *Surf. Coatings Technol.* **201**, 8966 (2007).
 - [32] I. Parkin, A. Kafizas, C. W. Dunnill, and G. Hyett, Combinatorial CVD: New oxy-nitride photocatalysts, *ECS Trans.* **25**, 1239 (2009).
 - [33] K. V. L. V. Narayanachari, D. Bruce Buchholz, E. A. Goldfine, J. K. Wenderott, S. M. Haile, and M. J. Bedzyk, Combinatorial approach for single-crystalline taon growth: Epitaxial β -Taon (100)/ α - Al_2O_3 (012), *ACS Appl. Electron. Mater.* **2**, 3571 (2020).
 - [34] M. Stüber, U. Albers, H. Leiste, K. Seemann, C. Ziebert, and S. Ulrich, Magnetron sputtering of hard Cr-Al-N-O thin films, *Surf. Coatings Technol.* **203**, 661 (2008).
 - [35] T. Miyata, Y. Mochizuki, and T. Minami, Combinatorial deposition by r.f. magnetron sputtering using subdivided powder targets as new development method for thin-film phosphors, in *Device and Process Technologies for Microelectronics, MEMS, and Photonics IV, Vol. 6037* (Society of Photo-Optical Instrumentation Engineers (SPIE), Bellingham, WA, 2005).
 - [36] A. Pélisson, Al-Si-N transparent hard nanostructured coatings, Ph.D. thesis, University of Basel, 2009.
 - [37] A. Pélisson, M. Parlinska-Wojtan, H. J. Hug, and J. Patscheider, Microstructure and mechanical properties of Al-Si-N transparent hard coatings deposited by magnetron sputtering, *Surf. Coatings Technol.* **202**, 884 (2007).
 - [38] A. Pélisson-Schecker, H. J. Hug, and J. Patscheider, Morphology, microstructure evolution and optical properties of Al-Si-N nanocomposite coatings, *Surf. Coatings Technol.* **257**, 114 (2014).
 - [39] M. Parlinska-Wojtan, A. Pélisson-Schecker, H. J. Hug, B. Rutkowski, and J. Patscheider, $\text{AlN}/\text{Si}_3\text{N}_4$ multilayers as an interface model system for $\text{Al}_{1-x}\text{Si}_x\text{N}/\text{Si}_3\text{N}_4$ nanocomposite thin films, *Surf. Coatings Technol.* **261**, 418 (2015).
 - [40] J. Musil, M. Šásek, P. Zeman, R. Čerstvý, D. Heřman, J. G. Han, and V. Šatava, Properties of magnetron sputtered Al-Si-N thin films with a low and high Si content, *Surf. Coatings Technol.* **202**, 3485 (2008).
 - [41] A. Bendavid, P. J. Martin, and H. Takikawa, The properties of nanocomposite aluminium-silicon based thin films deposited by filtered arc deposition, *Thin. Solid. Films* **420**, 83 (2002).
 - [42] E. Lewin, D. Loch, A. Montagne, A. P. Ehasarian, and J. Patscheider, Comparison of Al-Si-N nanocomposite coatings deposited by HIPIMS and DC magnetron sputtering, *Surf. Coatings Technol.* **232**, 680 (2013).

- [43] J. Patidar, A. Sharma, S. Zhuk, G. Lorenzin, C. Cancellieri, M. F. Sarott, M. Trassin, K. Thorwarth, J. Michler, and S. Siol, Improving the crystallinity and texture of oblique-angle-deposited AlN thin films using reactive synchronized HiPIMS, *Surf. Coatings Technol.* **468**, 129719 (2023).
- [44] J. Patidar, O. Pshyk, K. Thorwarth, L. Sommerhäuser, and S. Siol, Low temperature deposition of functional thin films on insulating substrates enabled by selective ion acceleration using synchronized floating potential HiPIMS, *Nat. Commun.* **16**, 4719 (2025).
- [45] L. Banko *et al.*, Effects of the ion to growth flux ratio on the constitution and mechanical properties of $\text{Cr}_{1-x}\text{—Al}_x\text{—N}$ thin films, *ACS Comb. Sci.* **21**, 782 (2019).
- [46] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/cqk9-d247> for more information on the composition calibration, Swanepoel code, nanoindentation measurements, hysteresis curves, additional TEM and XRD analysis, nitrogen polarizability, absorption coefficients, and XPS analysis.
- [47] M. Döbeli, C. Kottler, F. Glaus, and M. Suter, ERDA at the low energy limit, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **241**, 428 (2005).
- [48] A. Wiczorek, A. G. Kuba, J. Sommerhäuser, L. N. Caceres, C. M. Wolff, and S. Siol, Advancing high-throughput combinatorial aging studies of hybrid perovskite thin films via precise automated characterization methods and machine learning assisted analysis, *J. Mater. Chem. A* **12**, 7025 (2024).
- [49] R. Swanepoel, Determination of the thickness and optical constants of amorphous silicon, *J. Phys. E* **16**, 1214 (1983).
- [50] J. C. Manifacier, J. Gasiot, and J. P. Fillard, A simple method for the determination of the optical constants n , k and the thickness of a weakly absorbing thin film, *J. Phys. E* **9**, 1002 (1976).
- [51] D. Poelman and P. F. Smet, Methods for the determination of the optical constants of thin films from single transmission measurements: A critical review, *J. Phys. D. Appl. Phys.* **36**, 1850 (2003).
- [52] W. C. Oliver and G. M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, *J. Mater. Res.* **7**, 1564 (1992).
- [53] A. C. Fischer-Cripps, *Nanoindentation*, 3rd ed. (Springer, New York, 2011).
- [54] M. Fischer, M. Trant, K. Thorwarth, J. Patscheider, and H. J. Hug, A setup for arc-free reactive DC sputter deposition of Al-O-N, *Surf. Coatings Technol.* **362**, 220 (2019).
- [55] Malcolm W. Chase, Jr., *NIST-JANAF Thermochemical Tables*, 4th ed. (American Chemical Society, Washington, D.C./American Institute of Physics for the National Institute of Standards and Technology, New York, NY, 1998).
- [56] H. Schulz and K. H. Thiemann, Crystal structure refinement of AlN and GaN, *Solid State Commun.* **23**, 815 (1977).
- [57] P. Yang, H.-K. Fun, I. A. Rahman, and M. I. Saleh, Two phase refinements of the structures of $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ made from rice husk by Rietveld analysis, *Ceram. Int.* **21**, 137 (1995).
- [58] N. Ishizawa, T. Miyata, I. Minato, F. Marumo, and S. Iwai, A structural investigation of $\alpha\text{-Al}_2\text{O}_3$ at 2170 K, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **36**, 228 (1980).
- [59] H. Banno, T. Hanai, T. Asaka, K. Kimoto, and K. Fukuda, Electron density distribution and disordered crystal structure of 15R-SiAlON, $\text{SiAl}_4\text{O}_2\text{N}_4$, *J. Solid State Chem.* **211**, 124 (2014).
- [60] T. Ban and K. Okada, Structure refinement of mullite by the rietveld method and a new method for estimation of chemical composition, *J. Am. Ceram. Soc.* **75**, 227 (1992).
- [61] J. M. Niewehuizen and H. B. Haanstra, Microfractography of thin films, *Philips Tech. Rev.* **27**, 87 (1966).
- [62] R. N. Tait, T. Smy, and M. J. Brett, Modelling and characterization of columnar growth in evaporated films, *Thin. Solid. Films* **226**, 196 (1993).
- [63] S. Yip, The strongest size, *Nature (London)* **391**, 532 (1998).
- [64] A. S. Argon and S. Yip, The strongest size, *Philos. Mag. Lett.* **86**, 713 (2006).
- [65] C. S. Sandu, F. Medjani, R. Sanjinés, A. Karimi, and F. Lévy, Structure, morphology and electrical properties of sputtered Zr-Si-N thin films: From solid solution to nanocomposite, *Surf. Coatings Technol.* **201**, 4219 (2006).
- [66] M. Benkahoul, C. S. Sandu, N. Tabet, M. Parlinska-Wojtan, A. Karimi, and F. Lévy, Effect of Si incorporation on the properties of niobium nitride films deposited by DC reactive magnetron sputtering, *Surf Coatings Technol.* **188**, 435 (2004).
- [67] S. Vepřek, The search for novel, superhard materials, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **17**, 2401 (1999).
- [68] J. Musil, Hard nanocomposite coatings: Thermal stability, oxidation resistance and toughness, *Surf. Coatings Technol.* **207**, 50 (2012).
- [69] S. Vepřek, Recent search for new superhard materials: Go nano! *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **31**, 50822 (2013).
- [70] J. Procházka, P. Karvánková, M. G. J. Vepřek-Heijman, and S. Vepřek, Conditions required for achieving superhardness of $\geq 45\text{ GPa}$ in nc-TiN/a-Si₃N₄ nanocomposites, *Mater. Sci. Eng. A* **384**, 102 (2004).
- [71] S. Vepřek, P. Karvankova, and M. G. J. Vepřek-Heijman, Possible role of oxygen impurities in degradation of nc-TiN/a-Si₃N₄ nanocomposites, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct. Process. Meas. Phenom.* **23**, L17 (2005).
- [72] S. Vepřek and M. G. J. Vepřek-Heijman, Limits to the preparation of superhard nanocomposites: Impurities, deposition and annealing temperature, *Thin. Solid. Films* **522**, 274 (2012).
- [73] S. H. Sheng, R. F. Zhang, and S. Vepřek, Decomposition mechanism of $\text{Al}_{1-x}\text{Si}_x\text{N}_y$ solid solution and possible mechanism of the formation of covalent nanocrystalline AlN/Si₃N₄ nanocomposites, *Acta Mater.* **61**, 4226 (2013).
- [74] G. H. Liu, Z. Z. Zhou, Q. H. Wei, F. Fei, H. Yang, and Q. Liu, Preparation and tunable optical properties of ion beam sputtered SiAlON thin films, *Vacuum* **101**, 1 (2014).
- [75] F. Anjum, D. M. Fryauf, J. Gold, R. Ahmad, R. D. Cormia, and N. P. Kobayashi, Study of optical and structural properties of sputtered aluminum nitride films with controlled oxygen content to fabricate distributed Bragg reflectors for ultraviolet A, *Opt. Mater. (Amst)* **98**, 109405 (2019).
- [76] R. D. Shannon and R. X. Fischer, Empirical electronic polarizabilities of ions for the prediction and interpretation of refractive indices: Oxides and oxysalts, *Am. Mineral.* **101**, 2288 (2016).
- [77] A. Bikowski, A. Holder, H. Peng, S. Siol, A. Norman, S. Lany, and A. Zakutayev, Synthesis and characterization of (Sn,Zn)O alloys, *Chem. Mater.* **28**, 7765 (2016).
- [78] P. S. Bagus, G. Pacchioni, and F. Parmigiani, Surface core-level spectroscopy of Cu(100) and Al(100), *Phys. Rev. B* **43**, 5172(R) (1991).

- [79] G. M. Ingo, N. Zacchetti, D. della Sala, and C. Coluzza, X-ray photoelectron spectroscopy investigation on the chemical structure of amorphous silicon nitride ($a\text{-SiN}_x$), *J. Vac. Sci. Technol. A* **7**, 3048 (1989).
- [80] J. Musil, R. Jílek, M. Meissner, T. Tölg, and R. Čerstvý, Two-phase single layer Al-O-N nanocomposite films with enhanced resistance to cracking, *Surf. Coatings Technol.* **206**, 4230 (2012).
- [81] S. Frick, O. Pshyk, A. Müller, A. Wiczorek, K. Thorwarth, and S. Siol, Dataset: Accelerating the development of oxynitride thin films: A combinatorial investigation of the Al-Si-O-N system, Zenodo (2025), doi:[10.5281/zenodo.16992972](https://doi.org/10.5281/zenodo.16992972).