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# Thermal conductivity and mechanical properties of AIN-based thin films

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While many research activities concentrate on mechanical properties and thermal stabilities of protective thin films, only little is known about their thermal properties being essential for the thermal management in various industrial applications. Based on the  $3\omega$ -method, we show the influence of Al and Cr on the temperature dependent thermal conductivity of single-phase cubic structured TiN and single-phase wurtzite structured AlN thin films, respectively, and compare them with the results obtained for CrN thin films. The dc sputtered AlN thin films revealed a highly c-axis oriented growth for deposition temperatures of 250 to 700 °C. Their thermal conductivity was found to increase strongly with the film thickness, indicating progressing crystallization of the interface near amorphous regions during the sputtering process. For the 940 nm AlN film, we found a lower boundary for the thermal conductivity of  $55.3 \text{ W m}^{-1} \text{ K}^{-1}$ . By the substitution of only 10 at. % Al with Cr,  $\kappa$  significantly reduces to ~5.0 W m<sup>-1</sup> K<sup>-1</sup>, although the single-phase wurtzite structure is maintained. The single-phase face centered cubic TiN and  $Ti_{0.36}Al_{0.64}N$  thin films exhibit  $\kappa$  values of 3.1 W m<sup>-1</sup> K<sup>-1</sup> and 2.5 W m<sup>-1</sup> K<sup>-1</sup>, respectively, at room temperature. Hence, also here, the substitutional alloying reduces the thermal conductivity, although at a significantly lower level. Singlephase face centered cubic CrN thin films show  $\kappa$  values of 3.6 W m<sup>-1</sup> K<sup>-1</sup>. For all nitride based thin films investigated, the thermal conductivity slightly increases with increasing temperature between 200 and 330 K. This rather unusual behavior is based on the high defect density (especially point defects) within the thin films prepared by physical vapor deposition. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4953358]

## I. INTRODUCTION

The rapidly growing development of nitride based thin films has led to a great variety of applications. In addition to the very important field of protective coatings for the machining and forming industry or protective coatings for aerospace applications, nitrides are increasingly important not only for their specific (semi-) conducting and piezoelectric properties but also for their specific thermal properties.<sup>1</sup> For example, hexagonal closed packed (B4, wurtzite ZnS, abbreviated with w-) aluminum nitride thin films, a representative of the III-V semiconductors, have drawn great attention over the last decades due to their extremely high thermal conductivity combined with a rather low electrical conductivity (band gap of about 6 eV).<sup>2</sup> The additional excellent thermal stability and high mechanical properties of AlN are extremely attractive combinations for highly sophisticated applications, like functional thin films that also need to withstand friction and wear.<sup>2,3</sup> AlN is also an ideal candidate for surface acoustic wave devices, due to the outstanding optical and piezoelectric properties combined with a high acoustic velocity of up to 6000 ms<sup>-1</sup>.<sup>4,5</sup>

Face centered cubic (B1, NaCl, abbreviated with c-) titanium nitride and chromium nitride based coatings, which are

famous for their wear resistance, diffusion barrier abilities, and tribological properties, are examples of nitrides with a rather low thermal conductivity ( $\kappa$ ) with  $\kappa \sim 4.8 \text{ W m}^{-1} \text{ K}^{-1}$ .<sup>6,7</sup> These material combinations are ideal for the application as protective hard coatings in forming and tooling industry, leading to the great success of these coatings in these areas. Moreover, TiN thin films are used in solar cells, as high temperature diffusion barriers and Shottky or ohmic contact layers in microelectronic devices.<sup>8</sup>  $Ti_{1-x}Al_xN$  coatings, which are favored in various machining operations, exhibit a pronounced ability for self-adaption in mechanical as well as electrical and thermal properties upon annealing treatments (or during exposure to higher temperatures during application) because the single-phase face centered cubic (c) structure decomposes towards the stable constituents c-TiN and wurtzite structured (w) AlN.

The thermal conductivity of single-phase w-AlN (a single crystal would have just one grain/grain size) strongly depends on the oxygen content, grain size, and crystal orientation, and can be as high as  $320 \text{ Wm}^{-1} \text{ K}^{-1}$ .<sup>10</sup> Especially, the crystal structure of AlN (hexagonal wurtzite (B4), cubic zinc blend (B3), or face centered cubic rock salt (B1) like TiN and CrN) plays a major role in determining the thermal conductivity due to the primarily responsible heat conduction mechanism, the phonons. Four requirements are needed

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to obtain a high thermal conductivity: low atomic mass, strong bonding, simple crystal structure, and a low inharmonic behavior.<sup>11</sup> Furthermore, various studies clearly show that the growth techniques, the synthesis conditions, and the substrates used have a strong influence on the microstructure, the crystalline quality of the nitride coatings, and thus also on the derived mechanical and thermal properties.<sup>12–14</sup> Therefore, the reported values on the thermal conductivity of AIN thin films cover a tremendously huge range from  $\kappa \sim 5$  to 200 W m<sup>-1</sup> K<sup>-1</sup>.<sup>15–18</sup>

As the thermal conductivity is strongly influenced by the crystal structure, we need to mention that especially the crystal structure of various nitrides can be designed and modified by knowledge-based alloying with various elements, please see for example, the *ab-initio* as well as experimental studies reported in Refs. 21 and 22.

The thermal conductivity can be obtained by several measurement techniques,<sup>23</sup> where the  $3\omega$ -method overcomes the difficulties of black body radiation. It can be extended for measurements at different temperatures, and counts to the most reliable and accurate techniques.<sup>24–26</sup> Therefore, this technique was the choice of investigation in our studies.

For a detailed study on the influence of crystal structure, morphology, alloying effect, and deposition conditions on the thermal conductivity (obtained by the  $3\omega$ -method in the temperature range 200 to 330 K) of nitride coatings, we used the single-phase model systems: w-AlN, w-Al<sub>0.90</sub>Cr<sub>0.10</sub>N, face centered cubic c-CrN, c-TiN, and c-Ti<sub>0.36</sub>Al<sub>0.64</sub>N.

## **II. EXPERIMENTAL**

All AlN,  $Al_{1-x}Cr_xN$ , CrN, TiN, and  $Ti_{1-x}Al_xN$  thin films were prepared by reactive magnetron sputtering (AJA Orion 5 laboratory-scaled PVD) using a mixed Ar/N<sub>2</sub> glow discharge at a working pressure of 0.4 Pa (both gases with 99.999% purity). Prior to the depositions, the 100-oriented Si substrates  $(20 \times 7 \times 0.38 \text{ mm}^3, 10 \times 10 \times 0.38 \text{ mm}^3)$  were ultrasonically pre-cleaned in acetone and ethanol, and dc plasma-etched in a pure argon atmosphere at 6.0 Pa for 10 min. To minimize the effect of impurities, the deposition chamber was always evacuated to a base pressure of  $\leq 0.9$  mPa. To guarantee for a uniform morphology, structure, and chemical compositions of the coatings, the substrate-holder (6 in. diameter) was rotated with a frequency of 1 Hz during all depositions.

The aluminum nitride thin films are prepared by powering the 3 in. aluminum target (99.99% purity) with 11 W cm<sup>-2</sup> in dc mode using an Ar/N<sub>2</sub> flow rate ratio of 1/9. Eight different AlN thin films are prepared by varying the substrate temperature ( $T_{dep} = 250$ , 400, 500, 600, 700, or 800 °C) and the bias potential (floating for all temperatures and -75 V for  $T_{dep} = 250$  and 500 °C) in order to analyse their influences on the texture and thermal conductivity, respectively. Additionally, the AlN coatings prepared at  $T_{dep} = 250$  and 500 °C (with floating and -75 V dc bias) were grown with three different thicknesses between ~190 and 1360 nm. Thus, 17 different AlN films were prepared (for more details please see Table I).

The Al<sub>1-x</sub>Cr<sub>x</sub>N, CrN, TiN, and Ti<sub>1-x</sub>Al<sub>x</sub>N coatings were only prepared at  $T_{dep} = 500$  °C. The Al<sub>0.90</sub>Cr<sub>0.10</sub>N coating, exhibiting a thickness of 1180 nm, is prepared by simultaneous powering the 3 in. aluminum target with 11 W cm<sup>-2</sup> and the 2 in. chromium target with 2.5 W cm<sup>-2</sup>, and using an Ar/ N<sub>2</sub> flow rate ratio of 1/9 with floating potential of the substrates. CrN coatings are prepared with 12.1 W cm<sup>-2</sup> dc powering of the 2 in. chromium target (99.9% purity), an Ar/N<sub>2</sub> flow rate ratio of 4/6, and -50 V dc bias potential of the substrates, leading to 1070 nm thickness. The TiN coating, of 580 nm thickness, is prepared by dc powering the

TABLE I. Deposition parameters and chemical composition of the thin films prepared by PVD.

Specimen	$T_{dep}$ (°C)	Bias (V)	Al (at. %	Ti (at. %)	Cr (at. %)	N (at. %)	Thickness (nm)	Dep. rate (nm/min)
AlN	250						200	15.6
AlN	250						940	15.6
AlN	250						1320	15.6
AlN	250	-75					220	15.5
AlN	250	-75					490	15.5
AlN	250	-75					910	15.6
AlN	500						190	16.0
AlN	500		44.91			55.09	1050	16.0
AIN	500						1360	16.0
AIN	500	-75					200	14.9
AlN	500	-75					520	14.9
AIN	500	-75	43.31			56.69	940	14.9
AIN	300						2190	18.3
AIN	400						2000	16.7
AIN	600						1400	11.7
AIN	700						1340	11.2
AIN	800						1030	8.6
$Al_{1-x}Cr_xN$	500		44.64		4.91	50.45	1180	23.6
CrN	500	-50			50.13	49.87	1070	7.6
TiN	500			38.97		61.03	580	5.8
$Ti_{1-x}Al_xN$	500	-80	32.01	17.87		50.12	670	22.3

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2 in. titanium target (99.9% purity) with 12.1 W cm<sup>-2</sup> using an Ar/N<sub>2</sub> flow rate ratio of 8/2 and floating potential of the substrates. The 670 nm thin Ti<sub>0.36</sub>Al<sub>0.64</sub>N film is prepared by dc powering the 3 in. Ti<sub>0.33</sub>Al<sub>0.66</sub> compound target (99.9% purity) with 8.8 W cm<sup>-2</sup> in an Ar/N<sub>2</sub> gas mixture (Ar/N<sub>2</sub> flow rate ratio of 7/3) and applying -80 V dc bias to the substrates. All targets used are from Plansee Composite Materials GmbH. The deposition parameters for all coatings deposited are given in Table I.

The cross plane thermal conductivity of the thin films was determined applying a differential  $3\omega$  technique<sup>27</sup> using a home-built  $3\omega$  setup. In detail, the thermal conductivity of the thin films was determined by measuring two comparable samples on identical substrates with different thicknesses. For each  $3\omega$  experiment, a narrow metal strip serves as both the heater and the temperature sensor. This metal strip is heated by an oscillating current at a circular frequency  $\omega$ , which thus leads to a  $2\omega$  temperature oscillation of the heater, the sample, and the substrate. Due to the linear temperature dependence of the metallic heater, the  $2\omega$  temperature oscillation translates to a  $3\omega$  voltage oscillation, which is detected using a lock-in amplifier (7265, Signal Recovery). Prior to the thermal  $3\omega$  voltage detection, the first harmonic and all related higher harmonics are subtracted from the signal using an active filter design based on the technique suggested by Cahill et al.<sup>24,28</sup> As long as the thermal penetration depth within the substrate

$$\left|\frac{1}{q}\right| = \sqrt{\frac{D}{2\omega}},\tag{1}$$

is large compared to the heater half width *b* and at least five times smaller than the substrate thickness  $t_s$ , the amplitude of the temperature oscillation is given by<sup>24</sup>

$$\Delta T = \frac{P}{l\pi\kappa} \left[ -\frac{1}{2} \ln(2\omega) - \frac{1}{2} \ln\left(\frac{b^2}{D}\right) + \ln(2) - i\frac{\pi}{4} \right], \quad (2)$$

where P/l is the line power density, D is the thermal diffusivity of the substrate, and i is the imaginary unit. In the case that the thermal conductivity of the thin film  $\kappa_f$  is small compared to the thermal conductivity of the substrate, the film behaves as a simple thermal resistance and adds a frequency independent offset to the temperature oscillation. Thus, by measuring two comparable films with different thicknesses, the thermal conductivity of the films<sup>27</sup> can be determined from

$$\Delta T_f = \frac{P}{l\kappa_f} \frac{t_f}{2b},\tag{3}$$

where  $\Delta T_f$  is the frequency independent offset to the temperature oscillation and  $t_f$  is the differential film thickness.

The required metal heaters on top of the thin films were prepared by photolithography and sputtering. To avoid electrical contact between the heater and the sample, each specimen, except the AlN thin films, was additionally covered with a  $\sim$ 300 nm thin AlN layer prior to the heater deposition. Due to the chemical etching of the insulating AlN layers, the less labor-intensive lift off method with KOH based developers<sup>29–31</sup> could not be used to produce the heater structures. Instead, the ion etching technique had to be applied.

Figure 1 represents a schema of the pre-preparation working sequences of our specimens (AlN top layer on our nitride films with Si-substrate) for the  $3\omega$ -measurement. The procedure starts with the sputter deposition of a 5 nm Ti adhesion layer prior to the 75 nm thin Au layer, followed by the covering with a photoresist, the aligning of a photomask, the subsequent exposure to UV-light, and the final preparation of the heaters out of the Ti/Au layer via ion beam etching. Thereby, 75 nm thin Au heaters with a width of 15  $\mu$ m and a length of 2 mm are prepared on our AlN covered nitride films. The exact dimensions of the individual heaters, which are needed for an accurate determination of the thermal conductivity, are obtained by Dektak-profilometer measurements after the preparation steps.<sup>32</sup>

The phonon thermal conductivities of all investigated materials were calculated by subtracting an electronic contribution, determined using the Wiedemann-Franz law with a constant Lorenz number of  $L_0 = 2.44 \times 10^{-8} \text{ W} \Omega \text{ K}^{-233}$  and



FIG. 1. Working sequence of the photolithography (ion beam etching technique) to microstructure the specimens for the  $3\omega$  method.

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electrical resistivity data measured using the Van-der-Pauw method.<sup>34</sup>

The bi-axial stresses within our thin films are calculated via the modified stoney equation using the curvature of the coated Si substrates, obtained by a Nanovea PS50 profilometer.<sup>35</sup> By scanning electron microscopy (SEM, FEI Quanta 200 equipped with a field emission gun) and transmission electron microscopy (TEM, FEI TECNAI F20) of sample cross-sections, the growth morphology of our films is studied. Chemical compositions of our films are obtained by energy dispersive X-ray spectroscopy (EDS). Due to element-specific absorption, different accelerating voltages of 10, 15, and 20 kV were used.

The structure and crystalline phases of our thin films are analyzed by X-ray diffraction (XRD) in gracing incidence mode (Empyrean Panalytical diffractometer) with a Cu-K<sub> $\alpha$ </sub> ( $\lambda = 1.54$  Å) radiation source. Our coatings are also characterized for their mechanical properties (hardness (H) and indentation modulus (E)), which are evaluated throughout the loading and unloading segment of the indentation curves (using a UMIS Nanoindenter equipped with a Berkovich tip) according to the Oliver and Pharr method.<sup>36</sup>

#### **III. RESULTS AND DISCUSSION**

#### A. Residual stress analysis

Figure 2(a) clearly indicates that with increasing thickness, the stresses within our AlN thin films change from compression to tensile, and that with increasing deposition temperature or bias potential, the stresses are more compressive (or less tensile). The AlN thin films exhibit delamination effects and micro-crack formation as soon as the tensile stresses are in the range of about 0.5-1 GPa, which are obtained for thicknesses of ~1000 nm. The difference between the thermal expansion coefficient of AlN ( $\alpha \sim 4.35$  $\times 10^{-6}$  K<sup>-1</sup> at 300 K (Ref. 37)) and Si substrate ( $\alpha \sim 2.69$  $\times 10^{-6}$  K<sup>-1</sup> at 336 K (Ref. 38)) cannot explain the increasing compressive stresses (or decreasing tensile stress) with increasing deposition temperature. Increasing the deposition temperature from 250 to 500 °C would lead to thermally induced tensile stresses of about 0.3 GPa (due to the differential thermal expansion coefficient between film and substrate), after cooling down to room temperature.

In comparison, Figure 2(b) shows the stresses recalculated for the growth temperature, by simply subtracting the thermally induced stresses between deposition and room temperature. Thereby, we can clearly see that the compressive growth stresses significantly increase with increasing deposition temperature and especially with increasing the bias potential from floating to -75 V. However, the pronounced decrease in compressive stresses with increased layer thickness (in agreement with the earlier reports<sup>39</sup>) cannot be compensated by the increased deposition temperature or bias potential.

## B. Chemistry, structure, and morphology

The chemical composition of our coatings, obtained by EDS investigations, is summarized in Table I. Only for the TiN coating, the nitrogen content is not between 50 and



FIG. 2. (a) Residual stress versus obtained coating thickness for various AlN coatings deposited on Si(100). The specimens deposited at 250 and 500 °C are labeled with yellow full symbols and black open symbols, respectively. The applied bias potentials (-75 V/floating potential) are indicated with dashed and solid lines. (b) Re-calculated residual stress (by subtracting the thermally induced stresses) versus obtained coating thickness for various AlN coatings deposited on Si(100). The specimens deposited at 250 and 500 °C are labeled with yellow full symbols and black open symbols, respectively. The applied bias potentials (-75 V/floating potential) are indicated with symbols and black open symbols, respectively. The applied bias potentials (-75 V/floating potential) are indicated with dashed and solid lines.

55 at. %, which we attribute to the difficulties of the EDS measuring technique. To simplify notations, all coatings are normalized to 50 at. % nitrogen, and based on the metal sublattice composition of the ternary nitrides, we refer to our coatings with AlN,  $Al_{0.90}Cr_{0.10}N$ , CrN, TiN, and  $Ti_{0.36}Al_{0.64}N$ .

The XRD patterns of our AlN thin films prepared at various deposition temperatures, see Fig. 3, reveal a pronounced c-axis orientation of their wurtzite structure for  $T_{dep} = 250$ , 400, and 500 °C. The coating prepared at 600 °C already exhibits a more random orientation as also 101 oriented grains can be detected. For the even higher deposition temperatures of 800 °C, only an XRD-amorphous structure is obtained and the coating thickness significantly decreases to only 1030 nm suggesting that the high aluminum vapor pressure at the relatively hot substrate surface interferes with the crystal growth (see also the decreasing growth rate for deposition temperatures  $\geq 300$  °C).



FIG. 3. Structural evolution of the AIN coatings with increasing deposition temperature ( $T_{dep} = 250, 400, 500, 600, and 800 \,^{\circ}$ C). All coatings were deposited with floating bias potential. The  $2\theta$  peak positions for standardized w-AIN ( $a_w = 3.11 \,\text{\AA}, c_w = 4.98 \,\text{\AA}$  (Ref. 42)) and Si (substrate) are labeled with hexagonal open green symbols and red triangular symbols.

The pronounced c-axis orientation of the w-AlN thin films prepared with the deposition temperatures below 600 °C is also the preferable orientation for high thermal conductivity in wurtzite-structured materials.<sup>40,41</sup> Comparing the XRD pattern obtained in Bragg Brentano mode, Fig. 3, with that obtained in gracing incidence configuration, Fig. 4, suggests that with increasing coating thickness, the orientation of the w-AlN film changes to a more random configuration. Within the gracing incidence mode, only the outer most region of the w-AlN thin film contributes to the XRD pattern, whereas in Bragg Brentano mode, the entire coating contributes.



FIG. 4. XRD-patterns (gracing incidence configuration) recorded for AlN,  $Al_{0.90}Cr_{0.10}N$ , CrN, TiN, and  $Ti_{0.36}Al_{0.64}N$  deposited at 500 °C. The AlN coating, 1360 nm thin, is prepared with floating potential. The  $2\theta$  peak positions for standardized c-TiN ( $a_c = 4.22$  Å (Ref. 43)), c-CrN ( $a_c = 4.15$  Å (Ref. 44)), c-AlN ( $a_c = 4.05$  Å (Ref. 45)), and w-AlN ( $a_w = 3.11$  Å,  $c_w = 4.98$  Å (Ref. 42)) are labeled with solid blue squares, solid red squares, solid black squares, and open green hexagonal symbols.



FIG. 5. SEM cross sectional micrographs in the as deposited state of AlN (a),  $Al_{0.90}Cr_{0.10}N$  (b), TiN (c),  $Ti_{0.36}Al_{0.64}N$  (d), and CrN (e) prepared at  $T_{dep} = 500$  °C. The AlN thin film is prepared with floating potential.

By alloying 10 at. % Cr at the metal sublattice of AlN, the single-phased wurtzite structure is remained but the orientation becomes even more random, see Fig. 4. Contrary to these two coatings, w-AlN and w-Al<sub>0.90</sub>Cr<sub>0.10</sub>N, the CrN, TiN, and Ti<sub>0.36</sub>Al<sub>0.64</sub>N coatings clearly crystallize with a single-phase cubic structure.

SEM fracture cross sections of the coatings prepared at 500 °C clearly suggest for a dense growth morphology and smooth surfaces, see Fig. 5. Especially, the smooth surfaces are highly important for accurate  $3\omega$  measurements and an ideal preparation of the necessary Au-layer heaters. The AIN coating, due to its generally pronounced c-axis orientation, reveals an almost textbook-like columnar growth, Fig. 5(a). This slightly changes when alloying with Cr, as thereby also the preferred growth orientation is reduced, Fig. 5(b). Contrary, the single-phase cubic structured CrN, TiN, and Ti<sub>0.36</sub>Al<sub>0.64</sub>N coatings exhibit a random oriented growth morphology with short columns, see Figs. 5(c), 5(d), and 5(e), respectively.

### C. Mechanical properties

Figure 6 shows the hardnesses and indentation moduli of our single-phase cubic structured CrN, TiN, and Ti<sub>0.36</sub>Al<sub>0.64</sub>N coatings in comparison to the single-phase wurtzite structured Al<sub>0.90</sub>Cr<sub>0.10</sub>N and AlN coatings, prepared at 500 °C. Here, we need to mention that especially the TiN and Ti<sub>0.36</sub>Al<sub>0.64</sub>N coatings are rather thin with only 580 and 670 nm, whereas the other coatings are nearly twice as thick with values between 1070 nm and 1360 nm, see also Table II. Consequently, especially the hardness values for TiN and Ti<sub>0.36</sub>Al<sub>0.64</sub>N coatings are slightly underestimated. For these two samples, the maximum indentation depth was slightly above 1/10 of the coating thickness. Especially, the w-AlN coating, prepared at 500 °C with floating potential, which exhibits a pronounced c-axis oriented growth, has with 23.9 GPa a hardness comparable to the single-phase cubic TiN and CrN coatings. By the small addition of only 10 at. % Cr to the metal sublattice, the hardness slightly decreases from  $\sim$ 23 GPa to 21 GPa, which can be attributed to the change in preferred growth orientation from pronounced 0001 to a more random like. Furthermore, the



FIG. 6. Hardness (H-blue full symbols) and indentation modulus (E-red open symbols) on Si substrate in the as deposited state of AlN,  $Al_{0.90}Cr_{0.10}N$ , CrN, TiN, and  $Ti_{0.36}Al_{0.64}N$  at  $T_{dep} = 500$  °C. The AlN thin film is prepared with floating potential.

composition-induced changes in electronic structure also lead to decreasing bulk moduli with increasing Cr-content.<sup>46</sup>

Our wurtzite structured AlN coatings exhibit comparable hardness and indentation moduli for the different deposition temperatures, see Fig. 7, as long as the preferred orientation is 001 (c-axis oriented). The difference of about 2 GPa in hardness between the AlN coatings prepared at 250 and 500 °C nearly corresponds to the obtained different compressive stresses for these coatings; please compare Figs. 2(b) and 7. The coatings prepared at 600 and 800 °C, which are more random oriented or are even XRD amorphous, exhibit smaller indentation moduli and hardnesses.

The 001 orientation is the stiffest orientation,<sup>47</sup> as can be seen by the indentation moduli for the pronounced 0001oriented AlN thin film (prepared at  $T_{dep} = 500$  °C) with respect to the more random oriented AlN film (prepared at  $T_{dep} = 600$  °C) or the XRD-amorphous film (prepared at  $T_{dep} = 800$  °C).

#### **D.** Thermal conductivity

The film thermal conductivity can be calculated (Eq. (3)) from differential  $3\omega$ -measurements by determining the difference of the in-phase temperature oscillations of two experiments on a sample and reference sample at constant temperature, respectively. Figure 8 shows the measured amplitude of the in-phase<sup>24</sup> temperature oscillation of two AlN samples of different thicknesses as a function of frequency at a temperature of 295 K. The red circles and the gray squares



FIG. 7. Hardness (H-blue full symbols) and indentation modulus (E-red open symbols) on Si substrate in the as deposited state of AlN ( $T_{dep} = 250$ , 300, 400, 500, 600, 700, and 800 °C). The cubic symbols refer to floating potential, whereas the round symbols refer to -75 V bias potential.

correspond to the data obtained for the 940 nm and 200 nm thin AlN films, respectively, which were deposited at 250 °C and floating bias potential onto a Si substrate. For evaluation of  $\kappa_f$ , only the region where the in-phase temperature oscillation was found to be linear in logarithmic frequency was taken into account. The neglected regions are hatched in Fig. 8.

Contrary to the expectation, within the linear region, the data for the 940 nm and 200 nm films are almost identical. This indicates that the total thermal resistance, consisting of contributions from thermal boundary resistances (heater to film, film to substrate, and substrate to thermal bath), the substrate, and the film, are comparable.

Here, we want to mention that several measurements on other AlN films revealed actually higher thermal barriers for the thinner films than for the thicker ones. The reason for this unexpected behavior is the different thicknesses of amorphous-like regions (with lower thermal conductivity) near the interface to the Si substrate, identified by detailed TEM cross-sectional studies. As an example, Fig. 9 shows TEM images of the cross section for two significantly different thick AlN thin films. The amorphous-like layer has a thickness of about 15 nm to 20 nm for the thick AlN coating (Fig. 9(a)), but more than 80 nm for the thinner AlN sample (Fig. 9(b)). Details of the amorphous regions, by HRTEM investigations, are presented in Figs. 9(c) and 9(d). The reason for the different thicknesses of the amorphous-like layer near the interface can be found in the different processing times during the sputtering procedure. Pan et al.<sup>18</sup>

TABLE II. Elastic modulus, *E*, Poisson ratio,  $\nu$ , theoretical mass density,  $\rho_{\text{theor}}$ , speed of sound,  $v_s$ , Debye temperature,  $\theta_D$ , and phonon thermal conductivity at RT,  $\kappa_{ph}^{RT}$ . More detailed information on the shown values can be found in the Appendix.

Sample	E (GPa)	ν	$\rho_{\text{theor}}  (\text{kg/m}^3)$	<i>v</i> <sub>s</sub> (m/s)	$\theta_{\mathrm{D}}\left(\mathrm{K}\right)$	$\kappa_{ph}^{RT}  (\mathrm{W}  \mathrm{m}^{-1}  \mathrm{K}^{-1})$
TiN	259	0.25 (Ref. 50)	5400	5655	804	2.15
TiAlN	242	0.25	4233	6174	907	2.48
CrN	258	0.28 (Ref. 51)	5900	5756	822	3.44
AlCrN	234	0.21	3457	6237	845	4.74 (6.22 ann.)
AlN	273	0.21 (Ref. 52)	3260	6937	943	55.3 (940 nm)



FIG. 8. In-phase temperature oscillations as a function of the oscillator  $(1\omega)$  frequency of two AlN thin films at 295 K. The line power density during both measurements was fixed to 3 W/m. The red circles and the gray squares are the data obtained for the 940 and 200 nm thin AlN film, respectively. The black line corresponds to a simulation of a bare Si substrate (see text).



FIG. 9. Cross sectional TEM BF image of (a) thick AlN coating and (b) thin AlN reference sample. High resolution pictures of the interface near regions of both coatings (c) thick AlN coating and (d) thin AlN reference sample. All coatings were deposited at 500 °C with floating potential.

also reported on the formation of amorphous layers in the interface near region and their effects on the thermal conductivity. For the thermally characterized films studied here, TEM investigations, however, showed distinctive dense columns.

In case, the film thermal conductivity was independent of the film thickness, the contribution of the film to the total thermal resistance increases linearly with its thickness. Since the contributions from thermal boundary resistances are independent of the film thickness, they could, as previously suggested by Cho *et al.*<sup>19</sup> and Su *et al.*,<sup>20</sup> be evaluated by studying a series of films with different thicknesses.

Since for the AlN films studied here, where the contribution of the interface near regions to the thermal resistance is strongly dependent on the film thickness, the thermal boundary resistances cannot be disentangled from our data. A lower boundary for the film thermal conductivity can, however, be evaluated by comparing the measured in-phase temperature oscillations to a simulation (Eq. (2)) of a bare Si substrate taking into account a thermal conductivity of 149 W m<sup>-1</sup> K<sup>-1</sup>, a specific heat of  $0.7 \text{ J g}^{-1} \text{ K}^{-1}$ , a density of 2.329 g m<sup>-3</sup>, a heater width of 15  $\mu$ m, and a line power density of 3 W m<sup>-1</sup>. As indicated in Fig. 8, the contributions of the films and the boundaries to  $\Delta T$  result in roughly 3.4 mK. Neglecting all thermal boundary resistances as well as separate contributions from amorphous regions, we evaluate a lower boundary of the thermal conductivity of 11.8 and 55.3 W m<sup>-1</sup> K<sup>-1</sup> for the 200 nm and the 940 nm film, respectively.

Figure 10 shows the phonon thermal conductivity of the w-Al<sub>0.9</sub>Cr<sub>0.1</sub>N thin film, before and after annealing as a function of temperature. The electronic contribution, determined employing the Wiedemann Franz law to measured room temperature resistivity data, was found to be negligible for both the cases. The phonon thermal conductivity of the w-Al<sub>0.9</sub>Cr<sub>0.1</sub>N thin film shows glasslike characteristics pointing to strongly increased boundary  $(\tau_B^{-1})$  and point defect scattering rates  $(\tau_D^{-1})$  as compared to the binary single crystalline AlN.<sup>10</sup> Indeed, the data for the w-Al<sub>0.9</sub>Cr<sub>0.1</sub>N thin film could nicely be simulated taking into account a Callaway model with the appropriate sound velocities and Debye temperatures (Table II) as well as fixing all other parameters but  $\tau_B^{-1}$ and  $\tau_D^{-1}$  to the values determined from the fitting to data of single crystalline AlN.<sup>10</sup> The determined parameters are summarized in Table III. For the as-cast film (Fig. 10, dashed red line), both  $\tau_B^{-1}$  and  $\tau_D^{-1}$  were found to be increased by several orders of magnitude. The best simulation for  $\kappa_{ph}$  of the annealed film (Fig. 10, dash-dotted gray line) showed a comparable  $\tau_B^{-1}$  but a strongly decreased  $\tau_D^{-1}$ . The main effect of the annealing procedure is thus found in decreasing the defect



FIG. 10. Thermal conductivity of a sputtered w-Al<sub>0.9</sub>Cr<sub>0.1</sub>N thin film, before and after annealing at 850 °C for 100 min, as a function of temperature. The data are compared to the thermal conductivity of single crystalline AlN,<sup>10</sup> analyzed employing a Callaway<sup>49</sup> fit (black line, Eq. (A4)). The dashed lines are simulations according to the Callaway model and fixing the phonon scattering parameters according to the fit to the AlN data. The fitting parameters are summarized in Table III. The uncertainty in the measured thermal conductivities was determined by propagating the uncertainties in the heater geometry, the film thickness, and the temperature dependent heater resistance and amounts to roughly 7% for the films shown here.

TABLE III.	Fitting	parameter	Callaway	model.
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Specimen	$D(1/K^4 s)$	B (1/s)	$U(1/K^2 s)$	α (-)	$N(1/K^2 s)$	v <sub>s</sub> (m/s)	$\theta_{\rm D}$ (–)
AlN	0.0015	$9.53 \times 10^{5}$	3330	2.7	0.02	6976	950
$Al_{1-x}Cr_xN$	9.8	$5.64 \times 10^{12}$	3330	2.7	0.02	6237	844
$Al_{1-x}Cr_xN$ ann.	0	$5.64\times10^{12}$	3330	2.7	0.02	6237	844

concentration. The severe differences in the phonon dispersion of w-AlN<sup>28</sup> and w-CrN<sup>48</sup> indicate a strong dependence of the phononic properties of Al<sub>1-x</sub>Cr<sub>x</sub>N on the Cr-content, *x*. To the first approximation, these effects were included to our simulations by fixing the Debye temperature and the speed of sound to the values determined from the indentation experiments (Table II). However, quantitative statements cannot be drawn from the employed Callaway analysis.

The measured thermal conductivities of the c-CrN, c-TiN, and c-Ti<sub>0.36</sub>Al<sub>0.64</sub>N thin film are summarized in Fig. 11. Our  $3\omega$ -measurements resulted in a thermal conductivity well below 10 W m<sup>-1</sup> K<sup>-1</sup> for all the films in the whole temperature range between 200 K and 330 K.  $\kappa_{ph}$ , indicated by symbols in Fig. 11, again was calculated by subtracting an electronic contribution (indicated by lines) according to the Wiedemann Franz law. All cubic thin films studied show glasslike phonon thermal conductivity pointing to strong phonon-boundary and -defect scattering in the materials. Despite the larger disorder on the metallic sublattice, the ternary c-Ti<sub>0.36</sub>Al<sub>0.64</sub>N shows a higher phonon thermal conductivity than its binary counterpart TiN. This points to considerable changes in the phonon spectrum upon substitution, which is also reflected in the higher Debye temperature of c-Ti<sub>0 36</sub>Al<sub>0 64</sub>N (Table II).

It is quite counter-intuitive that CrN shows a higher thermal conductivity than the TiN and the  $Ti_{0.36}Al_{0.64}N$  thin film. CrN consists of atoms with higher average mass compared to  $Ti_{0.36}Al_{0.64}N$ . Thus, a lower speed of sound would be expected (and is also observed compared to  $Ti_{0.36}Al_{0.64}N$ ). Moreover, XRD measurements revealed smaller grains for CrN. Thus, the observed high thermal conductivity might be



FIG. 11. Phonon thermal conductivity (symbols) of the cubic films  $(Ti_{0.36}Al_{0.64}N, TiN, and CrN)$  as a function of temperature, and electronic contribution (lines) derived as explained in the text. The error bars were determined by propagating the uncertainties in the heater geometry, the film thickness, and the temperature dependent heater resistance.

explained by a much lower defect concentration, or by weaker three-phonon Umklapp scattering.

### **IV. CONCLUSIONS**

In this work, w-AlN, w-Al<sub>0.90</sub>Cr<sub>0.10</sub>N, c-CrN, c-TiN, and c-Ti<sub>0.36</sub>Al<sub>0.64</sub>N thin films were deposited on 100oriented silicon substrates using a dc reactive magnetron sputtering system. In order to explore the thermal conductivity over a wide temperature range, the  $3\omega$ -method in the differential operation mode was used.

All thin films studied revealed dense microstructures with very smooth surfaces. In addition, TiN, CrN, and TiAlN coatings exhibit single phase cubic fcc structures, whereas the AlN-based films are crystallized in the wurtzite phase. The mechanical properties of the coatings deposited are in excellent agreement to these observations and further literature reports. The thermal conductivity of AlN thin films was found to increase strongly with the film thickness. Neglecting all thermal boundary resistances, we found a lower boundary of the thermal conductivity of 11.8 and  $55.3 \text{ Wm}^{-1} \text{ K}^{-1}$  for the 200 and 940 nm film, respectively. The reason was found by detailed highresolution TEM cross section studies on several AlN thin films. These investigations revealed that with increasing thickness of the amorphous region (at the interface to the silicon substrate), the thermal conductivity of the AlN thin films decreases.

By substitutional alloying of 10 at. % chromium to the metal sublattice of the w-AlN thin film, the thermal conductivity decreases to 5 W m<sup>-1</sup> K<sup>-1</sup>, while still keeping the single-phase wurtzite structure. This underlines the high influence of additional phonon scattering centers which are introduced by the chromium atoms. All studied cubic thin films show glass-like phonon thermal conductivity pointing to strong phonon-boundary and -defect scattering. TiN thin films exhibited a phonon thermal conductivity of ~2 W m<sup>-1</sup> K<sup>-1</sup> at room temperature, and again, substitutional alloying with ~64 at. % of Al increases the thermal conductivity to 2.3 W m<sup>-1</sup> K<sup>-1</sup>. The unexpected higher thermal conductivity of c-CrN compared to the Ti<sub>0.36</sub>Al<sub>0.64</sub>N thin film might be explained by weaker three-phonon Umklapp scattering.

The results obtained clearly highlight the enormous potential of physical vapor deposition in independently modifying structure and chemistry of nitride thin films to specifically design their thermal conductivity over a very wide range.

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## APPENDIX: CALLAWAY FITTING PARAMETERS

$$B = \sqrt{\frac{E}{6 - 3 \cdot \nu}},\tag{A1}$$

$$v_{\rm s} = \sqrt{\frac{B}{
ho}},$$
 (A2)

$$\theta_{\rm D} = \hbar \frac{v_{\rm s}}{k_{\rm B}} \left( 6\pi^2 \frac{N}{V} \right)^{\frac{1}{3}}.\tag{A3}$$

Bulk modulus, *B*, was calculated, using the elastic modulus, *E*, gained from the indentation experiments and literature data for the Poisson ratio  $\nu$ . By applying Eq. (A2) for the speed of sound, the theoretical density  $\rho$  (using lattice parameters obtained from the XRD measurements) was calculated. Combining Eqs. (A1) and (A2), the debye temperature  $\theta_D$  can be calculated.

$$\kappa_{\rm ph} = \frac{k_{\rm B}^4 \cdot T^3}{2 \cdot \pi^2 \cdot v_{\rm s} \cdot \hbar^3} \cdot \left[ \int_0^{\frac{\Theta_{\rm D}}{T}} \tau \cdot \frac{x^4 \cdot e^x}{(e^x - 1)^2} \cdot dx + \frac{I_2}{I_1} \right], \quad \text{with}$$

$$I_1 = \int_0^{\frac{\Theta_{\rm D}}{T}} \frac{\tau}{\tau_{\rm N}} \cdot \frac{x^4 \cdot e^x}{(e^x - 1)^2} \cdot dx,$$

$$I_2 = \int_0^{\frac{\Theta_{\rm D}}{T}} \frac{1}{\tau_{\rm N}} \cdot \left( 1 - \frac{\tau}{\tau_{\rm N}} \right) \cdot \frac{x^4 \cdot e^x}{(e^x - 1)^2} \cdot dx,$$

$$\tau^{-1} = \tau_{\rm N}^{-1} + \tau_{\rm D}^{-1} + \tau_{\rm B}^{-1} + \tau_{\rm U}^{-1} + \tau_{\rm ph-el}^{-1}.$$
(A4)

Normal processes are usually taken into account by

$$\tau_{\rm N}^{-1} = N\omega^a T^b,\tag{A5}$$

where *a* and *b* are typically set to 2 and 3 for group III-V materials. Defect scattering can be taken into account by Rayleigh scattering<sup>53</sup>

$$\tau_{\rm D}^{-1} = D \cdot \omega^4, \tag{A6}$$

and boundary scattering by a frequency independent scattering rate<sup>53</sup>

$$\tau_{\rm B}^{-1} = B. \tag{A7}$$

Slack and Galginaitis.<sup>54</sup> suggested an Umklapp scattering rate taken into account by

$$\tau_U^{-1} = U\omega^c T^d e^{-\frac{v_D}{\alpha T}}.$$
 (A8)

For 
$$c = 2$$
,  $d = 1$ , and  $T \ge \theta_D$ ,  $\tau_U^{-1}$  becomes

$$\tau_U^{-1} \propto \omega^2 \cdot T. \tag{A9}$$

This behavior was earlier published by Klemens.<sup>55</sup>

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