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Growth and properties of amorphous Ti-B-Si-N thin films deposited by hybrid HIPIMS/DC-magnetron co-sputtering from TiB₂ and Si targets

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Abstract

Amorphous nitrides are explored for their homogenous structure and potential use as wear-resistant coatings, beyond their much studied nano- and microcrystalline counterparts. (TiB₂)_{1-x}Si_xN thin films were deposited on Si(001) substrates by a hybrid technique of high power impulse magnetron sputtering (HIPIMS) combined with dc magnetron sputtering (DCMS) using TiB₂ and Si targets in a N₂/Ar atmosphere. By varying the sputtering dc power to the Si target from 200 to 2000 W while keeping the average power to the TiB₂-target, operated in HIPIMS mode, constant at 4000 W, the Si content in the films increased gradually from x=0.01 to x=0.43. The influence of the Si content on the microstructure, phase constituents, and mechanical properties were systematically investigated. The results show that the microstructure of as-deposited (TiB₂)_{1-x}Si_xN films changes from nanocrystalline with 2–4 nm TiN grains for x=0.01 to fully electron diffraction amorphous for x=0.22. With increasing Si content, the hardness of the films increases from 8.5 GPa with x=0.01 to 17.2 GPa with x=0.43.

Keywords: HIPIMS, Transmission electron microscopy (TEM), Amorphous, Thin films, TiBSiN, Hardness

1. Introduction

Transition metal (TM) nitrides are used in many applications due to their wide range of properties, including high hardness [1], mechanical wear resistance [2], high thermal stability [3, 4], and good oxidation resistance [5–8].

For these materials, research has been mainly focused on thin films of various structure; first studies on microcrystalline material, later single crystals followed by nanocrystalline materials as well as and nanocomposites.

Especially in the development of hard coatings for mechanical applications microstructural design is of great importance, and the correlation between structure and mechanical properties has been thoroughly studied. It is by now well established that the microstructure of coatings grown by plasma-assisted vapor deposition techniques can be designed during growth or by post-deposition annealing treatments [9].

Despite the sterling work carried out in this field almost no studies are directed to amorphous transition

metal nitride thin films. Yet, they are potentially attractive, for example, as wear-resistant coatings due to their homogeneous structure and lack of grain and column boundaries that can act as fast diffusion paths and deteriorate toughness properties of polycrystalline coatings [10].

We have chosen the Ti-Si-B-N system for exploring amorphous nitrides, first grown by arc-deposition [11]. Here, we report the growth and properties of amorphous (TiB₂)_{1-x}Si_xN thin films deposited using a hybrid powering setup, where the Si target is operated in a conventional DCMS mode and the TiB₂ target is operated in HIPIMS [12] mode.

HIPIMS has been shown to have merits over conventional sputtering, including increased film density [13–15] because of the high degree of sputtered material ionization (up to 90%) [16]. Up until now, few studies address synthesis of amorphous thin films using HIPIMS. Most of them concern C-based thin films: graphite-like-carbon (GLC) [17, 18], diamond-like-carbon (DLC) [19], CN_x [20], CF_x [21], and SiCN [22], but also magnetic multicomponent soft magnetic FINEMET-type alloys have been studied [23, 24], as well as amorphous oxide thin films including TiO₂ [25], Al₂O₃ [26], and transparent conductive oxides (TCO) [27].

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Our results for fully electron-diffraction amorphous $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$ thin films are compared to those very recently reported for amorphous arc evaporated Ti-Si-B-N coatings [11]. The influence of the Si content on the microstructure, phase constituents, and mechanical properties are systematically investigated using TEM, XRD, ERDA, XPS, and nanoindentation. We show that employing the HIPIMS technique, with its high degree of ionization and subsequent increased momentum transfer to the growing film, is indeed a favorable route for growth of dense amorphous multicomponent nitride thin films.

2. Experimental procedures

Amorphous $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$, $0.01 \leq x \leq 0.43$ thin films are grown in a CC800/9 CemeCon AG magnetron sputtering system described in detail elsewhere [28]. The targets are rectangular $8.8 \times 50 \text{ cm}^2$ Si and TiB_2 , symmetrically mounted with a 21° angle between the substrate normal and the normal to the targets and a target-to-substrate distance of 18 cm. Si(001) wafers, $30 \times 10 \text{ mm}^2$, are used as substrates. The substrates are cleaned and degreased in successive ultrasonic baths of acetone and ethanol, and blown dry in dry N_2 before being mounted in the growth chamber.

The system is thoroughly degassed before deposition, using a two-hours long heating cycle consisting of two steps. First, two resistive heaters are powered to 10 kW for 60 min, resulting in a substrate temperature $T_s = 600^\circ\text{C}$. Following this, the heating power is reduced to 6 kW (corresponding to $T_s \sim 400^\circ\text{C}$), and held for another 60 min to stabilize the temperature and reduce the background pressure. The heating power is kept at 6 kW during the deposition. The base pressure following the heating cycle is $< 2.3 \times 10^{-6}$ Torr (0.3 mPa). The total film deposition time is 60 min, leading to a film thickness of $\sim 1.3 \mu\text{m}$ (deposition rate $\sim 22 \text{ nm/min}$), as determined by scanning electron microscopy (SEM) of fracture cross-sections and confirmed by cross-sectional transmission electron microscopy (XTEM). The Ar-to- N_2 flow ratio is kept at 0.2 by setting the Ar flow at $400 \text{ cm}^3/\text{min}$ (sccm), while the N_2 flow is controlled by a feedback loop to maintain P_{tot} constant at 3.2×10^{-3} Torr (420 mPa).

Film growth is carried out with the Si target operated as a conventional dc magnetron with an average power $P_{\text{Si,DC}}$ increased in steps of 100 W from 200 to 600 W, 200 W from 600-1400 W, and a final deposition is done with $P_{\text{Si,DC}} = 2000 \text{ W}$. The TiB_2 target is powered in HIPIMS mode at an average power of 4 kW

(8 J/pulse, 500 Hz, 10% duty cycle). A pulsed substrate bias voltage, -60 V, is applied synchronously during the full $200 \mu\text{s}$ HIPIMS pulse. Between the HIPIMS pulses, the substrate is at floating potential. After deposition, the samples are allowed to cool to $< 100^\circ\text{C}$ before opening the chamber.

The elemental compositions of as-deposited films are determined by elastic recoil detection analysis with a time-of-flight and energy detector (TOF-E-ERDA) using a 36 MeV $^{127}\text{I}^{8+}$ beam incident at 67.5° relative to the sample surface normal with the detector at a 45° recoil scattering angle [29], and evaluated using the CON-TES code [30].

A Philips Bragg-Brentano diffractometer with a line focus Cu K_α X-ray source is used for film phase and structure analyses. θ - 2θ scans are acquired over the 2θ range from 10 to 110° . High resolution x-ray reflectivity (XRR) measurements are performed with $2\theta = 0.1$ - 1.5° in a parallel-beam configuration with 0.25° slits for precise positioning of the reflected peaks. The X'pert Reflectivity 1.3 software package from PANalytical B.V. is used to determine the density of the films by fitting the acquired data.

A FEI Tecnai G2 TF 20 UT scanning TEM (STEM), operated at 200 kV, is used for nanostructural analyses. Cross-sectional TEM (XTEM) samples are prepared by standard mechanical polishing and ion milling.

X-ray photoelectron spectroscopy (XPS) was performed with a Axis Ultra DLD spectrometer from Kratos Analytical, using a monochromatic $\text{Al(K}_\alpha)$ radiation ($h\nu = 1486.6 \text{ eV}$) at a system base pressure $< 2 \cdot 10^{-7}$ Pa. XPS survey scans and narrow spectra of the Ti2p, B1s, Si2p, N1s, and O1s core-levels were collected on surfaces that were previously sputter-cleaned for 2 min with 500 eV Ar^+ ions incident at an angle of 70° with respect to the surface normal, and rastered over an area of $3 \times 3 \text{ mm}^2$. The analysis area is $300 \times 700 \mu\text{m}^2$ and centred in the middle of the sputter cleaned region. The "0" of the binding energy (BE) scale is determined from the Fermi edge cut-off of the reference, clean-sputtered Ag foil, with an accuracy better than 0.05 eV. The position of the $\text{Ag3d}_{5/2}$ core level peak is verified to be 368.30 eV. To ensure very good energy resolution all core level (narrow energy range) spectra were acquired with the pass energy E_{pass} of 20 eV, that results in the full-width-at-half-maximum of the reference $\text{Ag3d}_{5/2}$ peak $\text{FWHM}(\text{Ag3d}_{5/2}) = 0.55 \text{ eV}$. $E_{\text{pass}} = 160 \text{ eV}$ that yields $\text{FWHM}(\text{Ag3d}_{5/2})$ of 2.00 eV was used for the survey (wide energy range) scans. Quantification is

Table 1: Elemental composition of the as-deposited films on Si(001) substrates as determined by TOF-E-ERDA. Values within parenthesis are measured with XPS. The values have been normalized to 100 at.%.

Ti (at.%)	B (at.%)	Si (at.%)	N (at.%)	O (at.%)	C (at.%)	Ar (at.%)	Composition
(12.9) 16.1	(33.5) 31.0	(0.3) 0.6	(43.0) 48.6	(8.8) 2.9	(1.5) 0.3	(-) 0.5	(Ti _{0.34} B _{0.66}) _{0.99} Si _{0.01} N _{1.02}
16.9	31.2	1.1	49.7	0.1	0.4	0.6	(Ti _{0.35} B _{0.65}) _{0.98} Si _{0.02} N _{1.01}
16.0	30.5	2.6	49.8	0.1	0.3	0.7	(Ti _{0.34} B _{0.66}) _{0.95} Si _{0.05} N _{1.01}
(11.4) 15.5	(33.7) 29.1	(3.5) 4.0	(49.3) 50.0	(1.6) 0	(0.5) 0.4	(-) 1.0	(Ti _{0.35} B _{0.65}) _{0.92} Si _{0.08} N _{1.03}
15.4	27.8	5.5	49.9	0.1	0.6	0.7	(Ti _{0.36} B _{0.64}) _{0.89} Si _{0.11} N _{1.02}
14.3	26.4	7.9	50.1	0	0.3	1.0	(Ti _{0.35} B _{0.65}) _{0.84} Si _{0.16} N _{1.03}
(9.9) 13.4	(28.3) 24.5	(9.8) 10.4	(49.7) 50.3	(1.6) 0	(0.7) 0.3	(-) 1.1	(Ti _{0.35} B _{0.65}) _{0.78} Si _{0.22} N _{1.04}
12.6	22.9	12.5	50.6	0	0.3	1.1	(Ti _{0.35} B _{0.65}) _{0.74} Si _{0.26} N _{1.05}
11.9	21.8	14.0	51.0	0	0.2	1.1	(Ti _{0.35} B _{0.65}) _{0.71} Si _{0.29} N _{1.07}
(7.1) 9.0	(19.7) 17.8	(20.4) 19.9	(51.1) 51.7	(1.2) 0	(0.5) 0.3	(-)1.3	(Ti _{0.34} B _{0.66}) _{0.57} Si _{0.43} N _{1.11}

performed with CasaXPS (version 2.3.16) software and based on peak areas from narrow scans compensated for (i) the energy-dependent transmission function of the spectrometer, and (ii) the effect of kinetic energy dependent electron mean free path. Sensitivity factors are supplied by Kratos Analytical Ltd. (library filename: casaXPS.KratosAxis-F1s.lib).

Hardness measurements were performed using a Hysitron TI-950 TriboIndenter equipped with a Berkovich 142.3° diamond probe, calibrated using a fused silica standard. For each sample, a minimum of 25 indents were made at an indentation depth of ~100 nm (<10% of the film thickness to avoid influence from the substrate), corresponding to a maximum applied load of 2 mN. The indentation procedure consisted of three steps: 1) loading to P_{max} during 5 s, 2) hold for 2 s, and 3) unloading during 5 s. The average hardness and reduced elastic modulus with standard deviation were determined using the method described by Oliver and Pharr [31] by fitting 75% of the unloading curve.

3. Results and discussion

Previous studies on Ti_{1-x}Al_xN thin films deposited by the hybrid technique used in this study, showed that high-AlN-concentration, single-phase NaCl-structure films with high hardness and low residual stress could be grown by sputtering Al in HIPIMS mode and Ti in DCMS mode, thus, under conditions where a pulsed Al⁺ metal-ion flux is superimposed on the continuous flux of Ti neutrals. It was also shown that reversing the power supplies, so that the Ti target was powered by HIPIMS and Al sputtered in DCMS mode, resulted in two-phase films with high defect densities [32–34]. High defect densities and ion bombardment that promotes near-surface mixing and effective distortion of

any emerging crystallites during growth, is favorable for synthesis of amorphous films. Such conditions are provided by an intense Ti⁺/Ti²⁺ metal-ion bombardment, therefore for this work, we chose to operate the TiB₂ target in HIPIMS mode to serve as the Ti ion source.

The elemental composition of the as-deposited films determined by TOF-E-ERDA is presented in Table 1 and schematically illustrated in Fig. 1 (filled symbols). In addition, the values determined by XPS for samples with $x=0.01$, 0.08, 0.22, and 0.43 are added for reference, both in the table and in the figure (open symbols). There is a linear correlation between the Si content in the films and an increasing Si-target power: Si contents go from $x=0.01$ with $P_{Si,DC}=200$ W to $x=0.43$ with $P_{Si,DC}=2000$ W. At the same time, B and Ti contents decrease. All films are slightly B understoichiometric, Ti/B=0.54±0.03, compared to the target composition (Ti/B=0.5), which can be explained by the heavy

Figure 1: (Color online) Elemental composition with respect to the Si target power. Open symbols are values determined by XPS, and closed symbols are values measured with TOF-E-ERDA, respectively.

$\text{Ti}^+/\text{Ti}^{2+}$ ion bombardment during growth that causes re-sputtering of lighter B atoms. The same B deficiency was found for ZrB_2 films deposited utilizing HIPIMS mode on a ZrB_2 -target [35]. However, the Ti/B ratio is not very far from the stoichiometric value, and we therefore use the notation $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$ for the films to reflect the nominal Ti and B fractions from the deposition.

All films are slightly N overstoichiometric with $\text{N}/(\text{Ti}+\text{B}+\text{Si})=1.01\text{--}1.11$, and an increase in N concentration with increasing Si, as expected for the preferred 3:4 stoichiometry of Si_3N_4 . Impurities consist of C, O, and Ar. The C level is <0.6 at.%, and the O level is <0.1 at.% for all films except the one with the lowest Si content ($x=0.01$), where the O concentration is 2.9 at.%. This is the result of a porous structure of the film, as evidenced by TEM and further discussed below. It is unlikely that the O has been incorporated during growth since no other films have such high O levels and the TOF-E-ERDA depth profile (not presented) shows a decreasing O concentration with increasing depth. The given value of 2.9 at.% is an average value taken over the probed depth (~ 300 nm). The Ar incorporation in the films is increasing with Si content and goes from 0.5 at.% with $x=0.01$ to 1.3 at.% with $x=0.43$.

The elemental composition varies between TOF-E-ERDA and XPS. For elemental analysis, it should be noted that quantification in XPS is limited to the surface region (5–10 nm) and affected by preferential resputtering of elements during cleaning with Ar^+ ions. TOF-E-ERDA is excellent for detection of lighter elements

Figure 2: XRD patterns from as-deposited $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$ with increasing Si content, $0.01 \leq x \leq 0.43$.

Figure 3: (Color online) XPS spectra of a) B1s, b) Si2p, c) Ti2p, and d) N1s, for as-deposited $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$ $0.01 \leq x \leq 0.43$ films.

such as B, N, O, C, and Ar. In general, XPS gives lower Ti contents and higher B contents in comparison with TOF-E-ERDA, while the Si and N contents are almost equal in both techniques. The large difference in O concentration in the film with $x=0.01$ (2.9 at.% by TOF-E-ERDA and 8.8 at.% by XPS) is explained by the surface sensitivity in XPS.

Fig. 2 shows the x-ray diffractograms for the $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$ films with $0.01 \leq x \leq 0.43$ in the 2θ range $10\text{--}110^\circ$. Si 002 and 004 substrate peaks are indicated in the figure. For all film compositions, there is a low intensity feature positioned around 14° . It is asymmetric in shape, its position changes with changing x-ray energy, and it is visible also when measuring a pure Si substrate, so we conclude that it is not a film peak but a feature due to Bremsstrahlung. Films grown with $0.01 \leq x \leq 0.08$ show a broad low-intensity peak around $2\theta \approx 43^\circ$. This peak can be attributed to either $\text{TiN}(002)$ at 42.6° [36], or $\text{TiB}_2(101)$ at 44.4° [37], but is positioned slightly closer to the TiN peak position. No other film diffraction peaks are visible over the entire 2θ range. Films with compositions $x=0.01, 0.08, 0.22$, and 0.43 were chosen for further characterization of the microstructure evolution since they span over a wide compositional range.

Fig. 3 shows typical XPS narrow region spectra for a) B1s, b) Si2p, c) Ti2p, and d) N1s as a function of the Si content, x . The B1s spectra for $x \leq 0.22$ contain two contributions, a low binding energy peak at 187.9 eV corresponding to the B-Ti bond in TiB_2 [38], and by far a more intense peak at 190.9 eV, accounting for $\sim 95\%$ of the total peak intensity, corresponding to B-N [38]. The B-Ti peak intensity decreases with increas-

ing x , and eventually, for $x=0.43$ only the B-N peak is present. This can be attributed to the decreasing Ti content as well as increasing N content in the films, as the Si content is increasing. Films with $x=0.43$ contain only 9 at.% Ti, which is exclusively bonded to N as will be discussed below. The low intensity of the B-Ti peaks for $0.01 \leq x \leq 0.22$ indicate that B is preferentially bonded to N in all films, even if sufficient amount of Ti is present. The B-N peak shifts slightly towards higher binding energies with increasing Si content from 190.9 eV for $x=0.01$ to 191.1 eV for $x=0.43$.

Fig. 3b) shows the Si2p signal consisting of a single peak corresponding to the Si-N bond [38]. The peak intensity clearly increases with increasing x , and the position changes slightly from 101.8 eV with $x=0.08$ to 102.0 eV with $x=0.43$. No peaks corresponding to Si-Ti bonds are found.

The Ti2p signal in Fig. 3c) consist of a $Ti2p_{1/2}$ - $Ti2p_{3/2}$ spin-orbit split doublet (i.e. one chemical state gives rise to a pair of peaks with 1:2 area ratio). The Ti2p signal is complex to deconvolute, nevertheless contributions due to Ti-B and Ti-Si bonds can be excluded based on the analyses of the B1s and Si2p spectra. For films with $x \leq 0.22$, low intensity B-Ti peaks are observed in the B1s spectra, but the amount Ti-B bonds is too low to be detected in the Ti2p spectrum. The $Ti2p_{3/2}$ contributions are present in the BE range from 454 to 460 eV, while $Ti2p_{1/2}$ features are present in the range 460-466 eV. In the discussion below we focus on stronger $Ti2p_{3/2}$ peaks, as their $Ti2p_{1/2}$ counterparts do not add any new information. For films with $x=0.01$, three components contribute to the $Ti2p_{3/2}$ signal: (i) a peak at 454.8 eV corresponding to Ti-N, (ii) a Ti-N satellite peak at 457.3 eV, and (iii) Ti-O peak at ~ 459 eV (Ti-N and Ti-O BE values from [39]). The origin of the satellite feature is widely discussed in the literature and several interpretations have been proposed including: intra-band transitions (shake-up events) [40], decrease in the screening ability of the core-hole remaining after photoionization [41], and structural effects [42]. For films with $x > 0.01$, the Ti-O contribution vanishes, in agreement with the decreasing O level in the films (see Fig. 1).

Our data indicate that the relative intensity of the main Ti2p lines from Ti-N with respect to the satellite structures decreases with increasing Si concentration: for films with $x \geq 0.22$ the satellite structure dominates the spectrum and with $x=0.43$ the original Ti-N signal can no longer be distinguished.

The N1s spectra in Fig. 3d) contain contributions from several components including N-Ti, N-Si, and N-B. Their presence is implied by the appearance of the

Ti2p, Si2p, and B1s spectra discussed above. The detail assignment of the particular contributions is complicated by the fact that they are all very close in terms of BE. Moreover, the reported BE values for each of the components (N-Ti, N-Si, and N-B) show a large spread on the order of ~ 1 eV [43]. The mean N1s BE values for the N-Ti (TiN), N-Si (Si_3N_4), and N-B (BN) bonds are 397.2 ± 0.24 eV, 398.0 ± 0.43 eV, and 398.25 ± 0.26 eV respectively. With $x=0.01$ the N1s spectrum is particularly simple to interpret as the N-Si component is missing. Satisfactory deconvolution into two contributions, with a lower BE peak at 397.3 eV and a high BE peak at 398.4 eV, can be obtained. Based on the NIST data base cited above the lower BE component is assigned to N-Ti bonds, while the high BE contribution is due to N-B. The area ratio is $\sim 1:2$, in agreement with the elemental composition data given in Table 1. With increasing Si content, the presence of a N-Si contribution that overlaps with N-Ti and N-B signals, complicates the detail analysis. It can be noted, however, that in the limit of the highest SiN content, i.e. $x=0.43$, the N1s spectra is expected to be dominated by the Si-N component. In fact, the BE of N1s peak for the $x=0.43$ sample is 398.0 eV, which corresponds very well with the mean value for the Si-N bond in Si_3N_4 found in NIST data base.

Fig. 4a) is a typical cross-sectional bright-field TEM (BF-XTEM) image, with b) corresponding selected area electron diffraction (SAED) pattern, and c) high-resolution TEM (HR-TEM) image of an as-deposited

Figure 4: a) BF-TEM image, b) SAED pattern, and c) HR-TEM image from an as-deposited $(TiB_2)_{1-x}Si_xN$ film with $x=0.01$.

(TiB₂)_{1-x}Si_xN film with $x=0.01$. The BF-XTEM image in Fig. 4a) reveals a 1.3 μm thick film with porous regions present as brighter strokes throughout the entire film thickness. The porosities are inclined with $\sim 12^\circ$ with respect to the surface normal. The SAED pattern in Fig. 4b) shows a strong diffraction ring corresponding to TiN(002) and two weaker ones: the inner one corresponding to TiN(111) and the outer to TiN(220) or TiB₂(11 $\bar{2}$ 0). In addition, there are two diffuse quarter-arc shaped regions with higher intensity and spacing ~ 3.65 Å present just at the outer part of the halo of the diffraction pattern. A SAED pattern with Si-substrate diffraction spots (not shown here) was used for alignment and made it possible to determine the tilt angle of the film features giving rise to the diffraction intensities to 12° with respect to the film surface normal. This angle is in good agreement with predictions following the tangent rule [44, 45], which states the relationship between the source (target) angle α to the average column inclination angle β to: $2\tan\beta = \tan\alpha$. A target mounted with $\alpha=21^\circ$ with respect to the substrate normal would then yield growth with an angle of 11° .

The HR-TEM image in Fig. 4c) reveals 2-4 nm-sized TiN nanocrystallites separated by equally thick layers of an amorphous, most likely B-rich, phase. The amorphous phase form ~ 2 nm-wide channels, which are separated by distances ~ 3 -4 nm, tilted with the same angle

Figure 5: BF-TEM image from a (TiB₂)_{1-x}Si_xN film with $x=0.43$.

Figure 6: HR-TEM and corresponding SAED for (TiB₂)_{1-x}Si_xN films with a) $x=0.08$, b) $x=0.22$, and c) $x=0.43$.

as the porosities that are visible in the BF-XTEM image. Thus, we conclude that the amorphous channels are the origin of the two diffuse quarter-arc shaped halos in the SAED pattern.

Fig. 5 is a BF-XTEM of an as-deposited (TiB₂)_{0.57}Si_{0.43}N film. It shows the typical structure of films with $x \geq 0.08$, which are smooth and homogeneous without the type of porosities that were seen for films with $x=0.01$ in Fig. 4a).

Fig. 6 shows HR-TEM and corresponding SAED patterns from films with a) $x=0.08$, b) $x=0.22$, and c) $x=0.43$. Films with $x=0.08$, contain 3-5 nm-sized TiN nanocrystallites (indicated by white circles) dispersed in an otherwise amorphous matrix. The SAED pattern shows one strong intensity ring corresponding to TiN(220) or TiB₂(11 $\bar{2}$ 0), and the same type of diffuse quarter-arc shaped features at the outerpart of the central halo of the diffraction pattern, as was observed for films with $x=0.01$ in Fig. 4b). Films with $x=0.22$ in Fig. 6b) and $x=0.43$ in Fig. 6c) are fully electron-diffraction amorphous as revealed by the broad and diffuse halos in the SAED patterns, and no indications of lattice fringes in HR-TEM.

Fig. 7 shows the nanoindentation hardness H , reduced elastic modulus E_r , and density of the as-deposited films as a function of Si content. The hardness increases from 8.5 ± 0.9 GPa with $x=0.01$ to 12.3 ± 1.4 GPa with $x=0.02$. The reduced elastic modulus follow the same trend with an increase from 109 ± 7 GPa to 130 ± 7 GPa, while the density is the same for both samples, 2.5 g/cm^3 . After this initial large rise in H , the hardness continues to increase almost linearly from 12.3 ± 1.4 GPa with $x=0.02$ to 17.2 ± 0.9 GPa with $x=0.43$. The reduced modulus follows the same trend with values ranging from 109 ± 7 GPa with $x=0.02$

Figure 7: (Color online) Nanoindentation hardness, reduced elastic modulus E_r , and density for as-deposited $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$ with Si content, $0.01 \leq x \leq 0.43$.

to 181 ± 6 GPa with $x=0.43$. The sample grown with $x=0.16$ deviates from the linear trend for both the hardness and modulus. The density shows a similar behavior. Here, there is an increase in density with increasing Si content from 2.50 g/cm^3 with $x=0.01$ and 0.02 to 2.86 g/cm^3 with $x=0.11$. This is followed by a decreased density, 2.71 g/cm^3 with $x=0.16$, and then a continued linear increase to a maximum value of 2.90 g/cm^3 with $x=0.43$. The density values are comparable to those reported for thin film amorphous Si_3N_4 ($2.60\text{--}3.00 \text{ g/cm}^3$) [46], but lower than the theoretical value, 3.20 g/cm^3 , given for crystalline Si_3N_4 [47].

Mechanical properties of amorphous thin films cannot be explained by the theoretical and empirical framework that has been established for their nanocrystalline counterparts. Effects like the Hall-Petch relation and its inverse counterpart, grain boundary sliding, and hindering of dislocation motion is not relevant in amorphous films that are grain-free. The limiting factor for the hardness is rather the stiffness of the amorphous network itself, which is dependent on the strength and number density of bonds in the system. A study on amorphous SiC showed that the hardnesses of amorphous samples are directly related to the number density of Si-C bonds in the films, and independent on the actual film composition [48].

The relatively large number of possible binary components in the Ti-B-Si-N system make it difficult to determine what bond, or what set of bonds, that are decisive for the hardness of the films. The XPS results show predominance of strong Ti-B, Ti-N, and Si-N bonds, but no weak Ti-Si bonds in the films, explaining the promising high hardness that increases with increasing Si concentration in the films.

4. Conclusions

Amorphous $(\text{TiB}_2)_{1-x}\text{Si}_x\text{N}$, $0.01 \leq x \leq 0.43$, thin films are grown in a hybrid coating system operated with high power impulse magnetron sputtering (HIPIMS) and a DC magnetron sputtering (DCMS) from TiB_2 and Si targets in a N_2/Ar atmosphere. Films with Si content $x=0.01$ are porous, and exhibit a structure which consists of 2-4 nm TiN nanocrystallites separated by BN-rich amorphous phase channels. With $x=0.08$ the TiN nanocrystallites are 3-5 nm with lower number density. Increasing the Si content to $x \geq 0.22$ yields fully electron-diffraction amorphous films. The low hardness, $H=8.5$ GPa, for films with $x=0.01$ is explained by the porous structure and high O impurity level. For dense films, the hardness increases with increasing Si content, going from 12.3 GPa with $x=0.08$ to 17.2 GPa with $x=0.43$.

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- [1] L. Shizhi, S. Yulong, P. Hongrui, Plasma Chemistry and Plasma Processing 12 (1992) 287.
- [2] P. Hedenqvist, M. Bromark, M. Olsson, S. Hogmark, E. Bergmann, Surface & Coatings Technology 63 (1994) 115.
- [3] A. Flink, T. Larsson, J. Sjölen, L. Karlsson, L. Hultman, Surface & Coatings Technology 200 (2005) 1535.
- [4] A. Hörling, L. Hultman, M. Odén, J. Sjölen, L. Karlsson, Journal of Vacuum Science & Technology A 20 (2002) 1815.
- [5] D. McIntyre, J. E. Greene, G. Håkansson, J.-E. Sundgren, W.-D. Münz, Journal of Applied Physics 67 (1990) 1542.
- [6] L. A. Donohue, I. J. Smith, W.-D. Münz, I. Petrov, J. E. Greene, Surface & Coatings Technology 94-95 (1997) 226.
- [7] A. Ingason, F. Magnus, J. S. Agustsson, S. Olafsson, J. T. Gudmundsson, Thin Solid Films 517 (2009) 6731.
- [8] P. Holubář, M. Jilek, M. Šíma, Surface & Coatings Technology 120-121 (1999) 184.
- [9] P. H. Mayrhofer, C. Mitterer, L. Hultman, H. Clemens, Progress in Materials Science 51 (2006) 1032.
- [10] R. Wiedemann, V. Weihnacht, H. Oettel, Surface & Coatings Technology 116-119 (1999) 302.
- [11] H. Fager, J. M. Andersson, J. Jensen, J. Lu, L. Hultman, Journal of Vacuum Science & Technology A 32 (2014) 061508.
- [12] V. Kouznetsov, K. Macák, J. M. Schneider, U. Helmersson, I. Petrov, Surface & Coatings Technology 122 (1999) 290.
- [13] A. P. Eghasarian, P. E. Hovsepian, L. Hultman, U. Helmersson, Thin Solid Films 457 (2004) 270.
- [14] J. Alami, P. O. Å. Persson, D. Music, J. T. Gudmundsson, J. Böhlmark, U. Helmersson, Journal of Vacuum Science & Technology A 23 (2005) 278.
- [15] M. Samuelsson, D. Lundin, J. Jensen, M. A. Raadu, J. T. Gudmundsson, U. Helmersson, Surface & Coatings Technology 205 (2010) 591.
- [16] J. Böhlmark, J. Alami, C. Christou, A. P. Eghasarian, U. Helmersson, Journal of Vacuum Science & Technology A 23 (2005) 18.
- [17] X. Zhang, P. Ke, A. Wang, M. Huang, K. H. Kim, Transactions of Nonferrous Metals Society of China 22 (2012) 740.
- [18] M. Huang, X. Zhang, P. Ke, A. Wang, Applied Surface Science 283 (2013) 321.
- [19] K. Sarakinos, A. Braun, C. Zilkens, S. Mráz, J. M. Schneider, H. Zoubos, P. Patsalas, Surface & Coatings Technology 206 (2012) 2706.
- [20] S. Schmidt, Z. Czirány, G. Greczynski, J. Jensen, L. Hultman, Journal of Vacuum Science & Technology A 31 (2013) 011503.
- [21] S. Schmidt, G. Greczynski, C. Goyenola, G. K. Guerguiev, Z. Czirány, J. Jensen, I. G. Ivanov, L. Hultman, Surface & Coatings Technology 206 (2011) 646.
- [22] C. Pusch, H. Hoche, C. Berger, R. Riedel, E. Ionescu, A. Klein, Surface & Coatings Technology 206 (2011) 119.
- [23] I.-L. Velicu, M. Kowalczyk, M. Neagu, V. Tiron, H. Chiriac, J. Ferenc, Materials Science and Engineering: B 178 (2013) 1329.
- [24] I.-L. Velicu, M. Neagu, H. Chiriac, V. Tiron, M. Dobromir, IEEE Transactions on Magnetics 48 (2012) 1336.
- [25] C. Nouvellon, M. Michiels, J. P. Dauchot, C. Archambeau, F. Laffineur, E. Silberberg, S. Delvaux, R. Cloots, S. Konstantinidis, R. Snyders, Surface & Coatings Technology 206 (2012) 3542.
- [26] E. Wallin, T. I. Selinder, M. Elfving, U. Helmersson, Europhysics Letters 82 (2008) 36002.
- [27] B. Szyszka, W. Dewald, S. K. Gurram, A. Pflug, C. Schulz, M. Siemers, V. Sittinger, S. Ulrich, Current Applied Physics 12 (2012) 2.
- [28] CemeCon, HiPIMS Sputter Coating System, < [http : //www.cemecon.de/index.html](http://www.cemecon.de/index.html) >, visited 3 Feb 2014.
- [29] J. Jensen, D. Martin, A. Surpi, T. Kubart, Nuclear Instruments and Methods in Physics Research B 268 (2010) 1893.
- [30] M. S. Janson, CONTES conversion of time-energy spectra - a program for ERDA data analysis, Internal Report, Uppsala University, 2004.
- [31] W. C. Oliver, G. M. Pharr, Journal of Materials Research 7 (1992) 1564.
- [32] G. Greczynski, J. Lu, J. Jensen, I. Petrov, J. E. Greene, S. Bolz, W. Kölker, C. Schiffrers, O. Lemmer, L. Hultman, Journal of Vacuum Science & Technology A 30 (2012) 061504.
- [33] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J. E. Greene, L. Hultman, Vacuum 86 (2012) 1036.
- [34] G. Greczynski, J. Lu, M. P. Johansson, J. Jensen, I. Petrov, J. E. Greene, L. Hultman, Surface & Coatings Technology 206 (2012) 4202.
- [35] M. Samuelsson, J. Jensen, U. Helmersson, L. Hultman, H. Högberg, Thin Solid Films 526 (2012) 163.
- [36] TiN, Powder Diffraction File TiN: 00-038-1420, JCPDS International Centre for Diffraction Data, 2010.
- [37] TiB₂, Powder Diffraction File TiB₂: 00-035-0741, JCPDS International Centre for Diffraction Data, 2010.
- [38] D. Briggs, M. P. Seah, Practical Surface Analysis, John Wiley & Sons, Inc., 1993.
- [39] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Eden Prairie, USA, 1992.
- [40] D. Jaeger, J. Patscheider, Journal of Electron Spectroscopy and Related Phenomena 185 (2012) 523.
- [41] A. Arranz, C. Palacio, Surface Science 600 (2006) 2510.
- [42] P. Prieto, R. E. Kirby, Journal of Vacuum Science & Technology A 13 (1995) 2819.
- [43] NIST X-ray Photoelectron Spectroscopy Database, Standard Reference Database 20, Version 4.1, < [http : //srdata.nist.gov/xps/](http://srdata.nist.gov/xps/) >, 2012.
- [44] J. M. Nieuwenhuizen, H. B. Haanstra, Philips Technical Review 27 (1966) 87.
- [45] A. G. Dirks, H. J. Leamy, Thin Solid Films 47 (1977) 219.
- [46] T. Aiyama, T. Fukunaga, K. Niihara, T. Hirai, K. Suzuki, Journal of Non-Crystalline Solids 33 (1979) 131.
- [47] M. W. Barsoum, Fundamentals of Ceramics, Taylor & Francis Group, 2003.
- [48] M. A. El Khakani, M. Chaker, A. Jean, S. Boily, J. C. Kieffer, Journal of Materials Research 9 (1994) 96.