Growth and characterization of TiN/SiN(001) superlattice films

Hans Söderberg^{a)} and Magnus Odén

Division of Engineering Materials, Luleå University of Technology, SE-971 87 Luleå, Sweden

Axel Flink, Jens Birch, Per O.Å. Persson, Manfred Beckers, and Lars Hultman

Thin Film Physics Division, Linköping University, SE-581 83 Linköping, Sweden

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We report the layer structure and composition in recently discovered TiN/SiN(001) superlattices deposited by dual-reactive magnetron sputtering on MgO(001) substrates. High-resolution transmission electron microscopy combined with Z-contrast scanning transmission electron microscopy, x-ray reflection, diffraction, and reciprocal-space mapping shows the formation of high-quality superlattices with coherently strained cubic TiN and SiN layers for SiN thickness below 7–10 Å. For increasing SiN layer thicknesses, a transformation from epitaxial to amorphous SiN_x ($x \geq 1$) occurs during growth. Elastic recoil detection analysis revealed an increase in nitrogen and argon content in SiN_x layers during the phase transformation. The oxygen, carbon, and hydrogen contents in the multilayers were around the detection limit (~0.1 at.%) with no indication of segregation to the layer interfaces. Nanoindentation experiments confirmed superlattice hardening in the films. The highest hardness of 40.4 ± 0.8 GPa was obtained for 20-Å TiN with 5-Å-thick SiN(001) interlayers, compared to monolithic TiN at 20.2 ± 0.9 GPa.

I. INTRODUCTION

Recent studies on TiN/SiN_x multilayers have shown that SiN layers can grow epitaxially on TiN layers.^{1–4} This gives rise to strong interfacial bonding and effective superlattice hardening, with hardness values higher than for both the monolithic constituents [TiN and SiN_x ($x \geq 1$)] and multilayers containing thicker, amorphous SiN_x (a-SiN_x) layers.^{1,4} TiN/SiN_x multilayers grown on oxidized Si substrates result in polycrystalline films, and for thin (~3 Å) SiN_x layers the typical columnar growth morphology for TiN is maintained.^{1,2} As the SiN_x layer thickness is increased, a-SiN_x starts to form, resulting in the growth of polycrystalline TiN layers composed of equiaxed grains. The highest reported hardness values for TiN/SiN_x multilayers are observed for SiN_x layer thicknesses on the order of 3–7 Å.^{1,3,5} This thickness is comparable to the thickness of the amorphous tissue phase that has been assumed to surround TiN nanocrystallites within TiN–SiN_x nanocomposites at the percolation threshold (10–20 vol% Si₃N₄).^{6–8} Here the maximum hardness is achieved at a Si content of 6–10 at.%, corresponding to a SiN_x tissue phase thickness of 1–2 mono-

layers (~2–4 Å).⁸ Outstanding questions for the TiN–SiN_x system are for the nature of the SiN_x layers in terms of structure and nitrogen content as a function of layer thickness. For the crystalline SiN (c-SiN) tissue phase, the degree of coherency to the TiN phase also needs to be determined.

In the present work, epitaxial TiN/SiN(001) superlattices and polycrystalline TiN/SiN_x multilayer films have been grown by dual-reactive magnetron sputtering. The nearly identical lattice parameters for MgO and TiN (4.213 and 4.242 Å, respectively^{9,10}) were used to obtain epitaxial single-crystal TiN films, as known from the literature.¹¹ To address the topics above, our depositions of superlattices and multilayers were made over a wide range of deposition conditions, including different layer thicknesses, substrate temperatures, and substrate bias voltages during SiN_x deposition.

II. EXPERIMENTAL PROCEDURES

Film deposition was carried out in a reactive dual-magnetron direct current (dc) sputtering system¹² utilizing computer-controlled shutters to achieve the layered structure. Targets consisted of pure titanium and silicon discs, with purities of 99.97% and 99.99%, respectively. Argon and nitrogen were used as working and reactive gas at partial pressures of 4.0 and 0.5 mTorr, respectively.

^{a)}Address all correspondence to this author.

e-mail: soderberg.hans@gmail.com

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Purity of both gases was 99.99999%. The base pressure in the chamber was always $<10^{-6}$ Torr before depositions commenced. The targets were run in a constant-current mode, fed with 0.8 and 0.2 A for the Ti and Si targets, respectively. Resulting deposition rates were ~ 1.5 Å/s for TiN and ~ 0.5 Å/s for SiN_x.

Single-crystal, (001)-oriented MgO ($10 \times 10 \times 0.5$ mm³) wafers were used as substrates. Before insertion in the deposition chamber, the substrates were ultrasonically cleaned in trichloroethylene, acetone, and isopropyl alcohol baths. Prior to deposition, the substrates were preheated in situ for 1 h at >800 °C. Using the described procedure, high-quality epitaxial TiN films have been grown as observed in low-energy electron diffraction⁴ and reflection high-energy electron diffraction¹³ studies. This confirms the formation of a high-quality MgO surface through annealing, which has previously been reported.¹⁴ In addition, the high temperature removes surface hydroxide and carboxide, a process that has been thoroughly studied in annealing experiments in air.¹⁵ The substrate temperature was controlled by a resistive heater positioned behind the substrate holder. All samples except those used for rate calibration were deposited with a 500-Å TiN template layer at 700 °C. After the template, 30 bilayers were deposited with varied deposition conditions. In addition, some samples were also grown to a total thickness of 0.5 μm for more reliable nanoindentation experiments.

The primary set of samples consisted of multilayers grown at 500 °C, -30 V bias, constant TiN layer thickness (~ 40 Å), and varying SiN_x layer thickness (1.5–25 Å). In addition, at 500 °C and constant TiN and SiN_x layer thicknesses, 40 and 5 Å, respectively, bias was varied between floating potential (~ -17 V) and -60 V. For the same layer thicknesses and a constant bias of -30 V, samples were also grown at 300, 500, and 700 °C. With a constant SiN_x layer thickness of 5 Å, at 500 °C, and -30 V bias, the TiN layer thickness was varied (5, 20, and 40 Å). Finally, two multilayer samples were grown for dedicated elastic recoil detection analysis (ERDA), as described in Table I. Each sample was constituted of six multilayer TiN/SiN_x stacks. In the Ω-series sample, the SiN_x layer thickness was kept low and the SiN_x-to-TiN layer thickness ratio was kept constant, while the number of interfaces for each stack was varied. Each subsequent stack was grown to higher thickness to account for the lower ERDA depth resolution with increasing probing depths. In the Γ-series sample, the ratio of SiN_x-to-TiN individual layers was varied, while keeping the total bilayer thickness constant.

X-ray reflection (XRR) measurements were conducted to determine the multilayer periods (Λ), i.e., bilayer thickness of the films, and also to confirm that the deposition rate calibrations were correct. The multilayer periods were calculated from the reflectivity peak positions

TABLE I. Design of TiN/SiN_x multilayer samples for elastic recoil detection analysis; Ω-series (left column) and Γ-series (right column).*

Ω-series		Γ-series	
A	Λ = 50 + 5 Å (TiN + SiN _x) N = 10 Λ Total thickness = 550 Å Λ = 70 + 7 Å (TiN + SiN _x)	F	Λ = 45 + 5 Å (TiN + SiN _x) N = 12 Λ Total thickness = 600 Å Λ = 25 + 25 Å (TiN + SiN _x)
C	N = 9 Λ Total thickness = 693 Å Λ = 90 + 9 Å (TiN + SiN _x)	H	N = 14 Λ Total thickness = 700 Å Λ = 5 + 45 Å (TiN + SiN _x)
E	N = 8 Λ Total thickness = 792 Å Λ = 60 + 6 Å (TiN + SiN _x)	I	N = 16 Λ Total thickness = 800 Å Λ = 35 + 15 Å (TiN + SiN _x)
B	N = 14 Λ Total thickness = 924 Å Λ = 80 + 8 Å (TiN + SiN _x)	G	N = 18 Λ Total thickness = 900 Å Λ = 15 + 35 Å (TiN + SiN _x)
D	N = 12 Λ Total thickness = 1056 Å Λ = 50 + 5 Å (TiN + SiN _x)	J	N = 20 Λ Total thickness = 1000 Å Λ = 45 + 5 Å (TiN + SiN _x)
A	N = 20 Λ Total thickness = 1100 Å TiN(001) template, 500 Å MgO(001) substrate	F	N = 22 Λ Total thickness = 1100 Å TiN(001) template, 500 Å MgO(001) substrate

*A–J indicate different multilayer stacks within the respective sample, for which the first and last multilayer stack have the same configuration. Λ equals the multilayer period, i.e., bilayer thickness. N equals the number of bilayer repeats.

and a procedure described elsewhere.¹⁶ The XRR studies were conducted on a Philips PW1729 diffractometer with θ – 2θ geometry and Cu K_α radiation. XRR simulations were carried out with the IMD extension¹⁷ under the XOP software.¹⁸ For high-resolution x-ray diffraction (HRXRD), we used a Philips four-axis materials research diffractometer (MRD) equipped with a primary monochromator utilizing a graded, parabolically bent multilayer mirror followed by a two-bounce Ge(220) monochromating crystal (producing Cu K_{α1} radiation). Reciprocal space mapping was made using a 15° asymmetrically cut two-bounce Ge(220) analyzer crystal.

Cross-sectional transmission electron microscopy (TEM) specimens were prepared by mechanical grinding and polishing. Low-angle Ar ion milling, in a Gatan PIPS ion miller, was used to obtain electron transparent specimens. TEM imaging was performed in a FEI Technai G² UT FEG operated at 200 kV for 1.9-Å point resolution. For scanning transmission electron microscopy (STEM) imaging a FEI (Eindhoven, The Netherlands) Titan 80-300 S/TEM microscope, operated at 300 kV was used to achieve better than 1.4-Å point resolution. A high-angle annular dark-field detector (HAADF) was used to obtain STEM images. A camera length of 300 mm was selected to provide sufficient contrast from the SiN_x layers.

Both ERDA samples were analyzed using a 347-MeV Au ion beam. The resulting energy-over-depth recoil spectra were transformed to depth resolved concentration

profiles using the KONZERD code. Additionally, all spectra were fitted with the SIMNRA computer code. Details on the experimental setup and the fitting procedure can be found elsewhere.¹⁹

The film hardness was evaluated with a Nanoindenter II instrument equipped with a diamond Berkovich indenter. Several different loads (2–10 mN) were used, and for each load at least 10 indents were made. The loading cycle consisted of two loadings to maximum load ($L_{\max}$) with an intermediate unloading to 10% $L_{\max}$. Hold periods were applied at the intermediate 10% $L_{\max}$ load to correct for any thermal drift and at the final $L_{\max}$ to reveal the presence of any creep. Hardness was obtained through the procedure developed by Oliver and Pharr.²⁰ From the indentation data generated for loads not influenced by the substrate, an average hardness value and its standard deviation were calculated.

III. RESULTS

All as-deposited films exhibited a number of peaks in XRR scans confirming a layered structure with a strong compositional modulation. The majority of samples thus showed two to four sharp reflectivity peaks and Kiessig fringes. Even for a SiN_x interlayer thickness as thin as ~1.5 Å, a multilayer peak was observed, though weak. Figure 1 shows the reflectivity curve with corresponding simulated curve from a sample grown at 500 °C. The sample was grown without a TiN template layer and with TiN and SiN_x layers of approximately equal thickness, 11 Å; hence the low intensity of the second Bragg reflection. The simulated^{17,18} curve matches the two peaks, and the resulting wavelength value is close to the expected one based on the deposition rate calibrations. Good agreement with the majority of the Kiessig fringes

FIG. 1. Measured (upper) and simulated (lower) x-ray reflectivity curves from a TiN/SiN_x multilayer film grown on MgO(001) at 500 °C. TiN and SiN_x layer thicknesses are ~11 Å. Curves are vertically separated for clarity and plotted against θ .

is also observed, resulting in an interfacial thickness of 1 Å, defined as the root-mean-square interfacial roughness and the interfacial width.¹⁷

Figure 2 shows the HRXRD diffractograms from the set of samples deposited at 500 °C with varying SiN_x layer thicknesses and constant TiN layer thickness (~40 Å). Also added is the diffractogram from the monolithic TiN film which exhibits two sharp peaks, corresponding to TiN 002 and MgO 002. With the introduction of SiN_x interlayers, already at thicknesses of ~2 Å the first indications of a first-order superlattice (SL) peak are observed around 40° 2 θ . As the SiN_x interlayer thickness increases, the first-order SL peak becomes more distinct. Simultaneously, second-order SL peaks at lower 2 θ angles are also observed. The formation of SL peaks is evidence of the growth of a highly repetitive layered structure with flat interfaces. In addition to the SL peaks, from a SiN_x thickness of 2.6 Å, low-intensity fringes of two different modulation periods are observed, the longer of these periods is marked with $\Delta 2\theta$ in the figure. For thicker SiN_x layers, only the longer fringe period is preserved. These fringes are so-called Pendellösung fringes,²¹ or finite-thickness fringes, originating from interference between the different sections within the film (i.e., multilayer, template layer, substrate) and their interfaces. The TiN 002 peak changes appearance with increasing SiN_x layer thicknesses. It changes from a very sharp, for monolithic TiN and for multilayers containing thin SiN_x interlayers, to a broad appearance as the SiN_x layers approach 13 Å. In addition, a small shift toward higher 2 θ values of the TiN 002 maximum intensity position occurs for samples with SiN_x layers of 2.6–5.5 Å thickness.

XRR and XRD curves from samples with varying

FIG. 2. HRXRD scans from a monolithic TiN(001) film and a series of TiN/SiN_x multilayers with increasing SiN_x layer thickness grown on MgO(001) at 500 °C. The interference fringe width ($\Delta 2\theta$) is marked and corresponds to the template layer thickness (see Sec. IV).

negative substrate bias, V_s , showed that $V_s = 30\text{--}40$ V produces the most distinct reflection and diffraction curves. However, only a slight degradation was seen for samples grown at floating potential (approximately -17 V) and $V_s = 50\text{--}60$ V. Figure 3 shows XRR curves from TiN/SiN_x multilayer grown at $T_s = 300$, 500, and 700 °C. All samples exhibit reflection peaks and intermediate Kiessig fringes, supporting the growth of a compositional modulation in the three cases. For the sample grown at 300 °C, the XRD curve display only SL peaks, suggesting lower interfacial quality. This is likely an effect of the reduced ad-atom mobility, which promotes amorphous phase formation. For $T_s = 500$ °C, both SL peaks and fringes are observed, indicating a film with higher crystalline order than for the 300 °C case. For $T_s = 700$ °C, peak broadening of TiN 002 occurs and XRR shows that both SL peaks and fringes, however less distinct, compare to the 500 °C case. These observations are consistent with the formation of a-SiN_x layers with low roughness, suggesting a lower stability for the c-SiN at 700 than at 500 °C.

FIG. 3. (a) X-ray reflection and (b) diffraction scans for TiN/SiN_x multilayers grown at 300, 500, and 700 °C. Layer thicknesses are 40 and 5 Å for TiN and SiN, respectively.

Figures 4(a) and 4(b) show the reciprocal-space maps (RSM) around the 002 and 113 MgO substrate peaks, respectively, from a superlattice film grown at 500 °C with TiN and SiN_x layer thicknesses of 40 and 5.5 Å, respectively. All observed intensity is well confined in reciprocal space, and no indication of any polycrystalline growth exists. In addition to the MgO 002 and TiN 002 primary peaks, SL peaks, Pendellösung fringes (P), and analyzer streaks (A) are also observed in the two RSMs. The RSM results indicate the growth of well-defined single-crystal films, i.e., superlattices. To further check the symmetry of the film in Fig. 4 (which shows one of the four 113 regions), 360° ϕ -scans over the asymmetric TiN 113 peak were performed. They revealed only four peaks symmetrically spaced, which is indicative of a single crystal, in our case, a TiN/SiN(001) superlattice.

Figures 5(a) and 5(b) show high-resolution TEM micrographs from TiN/SiN_x multilayers with 5.5-Å SiN(001) layers and 13-Å SiN_x layers, respectively. In Fig. 5(a), the crystalline TiN lattice is maintained from one layer to the next via the epitaxially stabilized SiN layers. These can be seen as brighter lines of contrast, apparently without an amorphous component. This observation confirms the single-crystal nature of the superlattice sample. The difference in contrast derives from the incoherent scattering strength of the present atoms and absorption effects. Interface strain is visible at the TiN/SiN(001) interfaces. It is suggested that the layers

FIG. 4. Reciprocal-space maps from a TiN/SiN(001) superlattice film with 5.5-Å thick SiN layers around the region of (a) the 002 orientation and (b) the 113 orientation. Superlattice peaks (SL), Pendellösung (P), and analyzer (A) streaks are marked. Axis units are reciprocal lattice units normalized with respect to the diameter of the Ewald sphere, $k_0 = 2(2\pi/\lambda)$, i.e., the theoretical maximum distance from the origin for a specific wavelength.

FIG. 5. Cross-sectional TEM micrographs from TiN/SiN_x multilayers containing (a) 5.5-Å SiN(001) and (b) 13-Å SiN_x layers, respectively. TiN layer thicknesses are ~40 Å.

are strained to accommodate for the epitaxial growth of under stoichiometric (with respect to Si₃N₄) SiN_x.

For a SiN_x layer thickness of 13 Å [Fig. 5(b)], amorphous interlayers begin to form, which results in the loss of the single-crystal template layer for each new TiN layer, see Fig. 2 where no SL peaks are observed at this SiN_x layer thickness. Consequently, a more or less polycrystalline film results, similar to earlier growth studies of TiN/SiN_x multilayers made on oxidized Si wafers.¹ As shown in Fig. 5(b), at 13 Å SiN_x, the layers grow amorphous. However, the initial atomic layers in each SiN_x layer exhibit epitaxial growth, and the transition to polycrystalline/amorphous phase occurs gradually with increasing SiN_x thickness.

STEM micrographs obtained from the layers next to the TiN(001) template layer are shown in Fig. 6. The overview image in Fig. 6(a) reveals that the first few TiN and SiN layers grow epitaxially on each other. Epitaxial growth was seen over the first five TiN layers with decreasing intensity. In the fifth layer, the rightmost grain assumes a completely different orientation, revealing the onset of TiN renucleation which gives rise to a mixed epitaxial/polycrystalline film nature. An atomic-resolution STEM image shows the first SiN(001) layer [Fig. 6(b)]. Because of the difference in atomic mass (*Z*) and the contribution from mass contrast (*Z*²), the SiN layer contrast is weak. Nevertheless, the epitaxial nature of the SiN layer is indisputable. A misfit dislocation in the top of the layer is identified, supporting the TEM

FIG. 6. Atomic resolution STEM images from a TiN/SiN_x multilayer film with 13-Å thick SiN_x layers in (a) overview showing also the TiN(001) template layer (bottom), and (b) atomic resolution of a region with epitaxial growth marked in (a) containing also a misfit dislocation (denoted by the white “T”).

observations and the assumption of a small lattice mismatch between TiN and c-SiN.

Figure 7 shows the ERDA concentration profiles as derived from the KONZERN code. The Ω-series depicted in Fig. 7(a) exhibits a low overall silicon content and a more or less crystalline structure; it also shows oxygen and other impurity contaminations around and below 0.1%, independent of the number of interfaces. The nitrogen concentration in all six stacks of the multilayer sample was ~50% ± 1%, which corroborates our previous assignment of stoichiometric SiN in its strain-stabilized cubic polytype. In contrast, for the Γ-series with sections containing c-SiN and a-SiN_x, an increase in silicon concentration is clearly correlated with a nitrogen increase, as shown in Fig. 7(b). Also, the nitrogen concentration lies considerably above 50% (*x* > 1), pointing toward formation of amorphous Si₃N₄. In addition, argon shows a strong peaking for highest silicon contents, possibly due to easier argon incorporation from the sputtering gas into an amorphous SiN_x matrix of lower density compared to c-SiN and TiN. We assume that the amorphous SiN_x phase has the composition Si₃N₄ since growth was carried out in a highly N₂-rich ambient. This assumption was checked by the growth, under the same conditions, of a 500-nm-thick SiN_x layer where the composition was subsequently determined by ERDA to be Si₃N₄.

FIG. 7. Elastic recoil detection analysis concentration depth profiles calculated by the KONZIRD code. Dashed vertical bars indicate the six stacks of each sample, as defined in Table I. In (a) the Ω -series, with a constant TiN/SiN_x ratio, varying the number of interfaces, and keeping a low SiN_x concentration, and (b) the Γ -series with a constant bilayer thickness and varying the SiN_x content.

Table II shows the quantified ERDA results from both samples as obtained from fitting the experimental spectra by SIMNRA. The alternating TiN/SiN_x single layers were disregarded in the analysis; instead, a homogeneous mixture of Ti and Si within each of the six-layer stacks was assumed. The table shows the average values for each stack. It is notable that for the Ω -series, the impurity—oxygen, carbon, hydrogen, and argon—levels are constant over the whole thickness while the number of TiN–SiN_x interfaces is increased from 8 to 20. Segregation of impurities toward these interfaces can hence be excluded. For the Γ -series, as already seen from the concentration profiles in Fig. 7, the nitrogen concentration increases with SiN_x content. However, an exact calculation of x in the SiN_x is hindered by the up to 2% Ar incorporation that is assumed to be incorporated in the a-SiN_x layers, which are of lower density than TiN.

In Fig. 8(a), the hardnesses from TiN/SiN_x multilayer samples with varying SiN_x layer thickness are shown. These films are grown with ~ 40 Å TiN, at 500 °C, and with a bias of -30 V. For comparison, hardness data on polycrystalline multilayers deposited on oxidized Si wafers from our earlier work¹ are also added. In this study, as well as in the previous study,¹ the hardness is higher for the multilayers compared to the monolithic films. This is in agreement with the large number of reports throughout the last two decades concerning various superlattice films with strong compositional modulation for coherently strained layers of phases with different shear moduli.^{22–24} In the set of samples grown in this study, the highest hardness is observed for a SiN_x layer thickness of 7.5 Å, reaching 34.0 ± 2.4 GPa. With the formation of a-SiN_x and the growth of polycrystalline TiN layers in a “nanobrick-like”¹ structure, the hardness drops to some

TABLE II. Fitted elastic recoil detection analysis depth profile concentrations as calculated by SIMNRA.

Sample	Thickness (10 ¹⁵ at./cm ²)	Ti (Å)	Ti (at.%)	Si (Å)	Si (at.%)	N (at.%)	H (at.%)	C (at.%)	O (at.%)	Ar (at.%)
Ω -series	15	0	24	0	...	...	23	5	48	...
	700	50	46	5	3.5	50.08	0.05	0.05	0.1	0.2
	750	70	46	7	3.5	50.03	0.05	0.05	0.15	0.2
	850	90	45.85	9	3.5	50.25	0.05	0.05	0.1	0.2
	950	60	45.62	6	3.5	50.5	0.05	0.05	0.1	0.2
	1200	80	44.8	8	3.6	51.11	0.05	0.05	0.15	0.1
	1350	50	44.5	5	3.6	51.44	0.05	0.05	0.15	0.2
	330	500	50	0	...	49.95	...	0.05	...	...
Γ -series	15	0	25	0	...	...	20	5	50	...
	650	45	44.59	5	5	50.015	0.025	0.05	0.1	0.22
	750	25	26.24	25	19.2	52.11	0.25	0.05	0.15	2.0
	800	5	12.2	45	32.89	52.46	0.3	0.05	0.1	2.0
	950	35	36.3	15	11.1	51.555	0.025	0.2	0.1	0.9
	1050	15	18.2	35	24.4	54.01	0.15	0.05	0.19	3.0
	1300	45	44	5	4	51.456	0.025	0.02	0.19	0.3
	350	500	50	0	...	49.95	...	0.05	...	...

FIG. 8. (a) Nanoindentation hardness of TiN/SiN(001) superlattice films grown on MgO (marked with diamonds) compared with polycrystalline TiN/SiN_x multilayer samples grown on Si (see Ref. 1) (squares) as a function of SiN_x layer thickness. (b) Hardness as a function of TiN layer thickness (top x axis) with SiN_x thickness constant at 5 Å, and hardness as a function of negative substrate bias, V_s (lower x axis) with constant TiN and SiN_x thickness of 40 and 5 Å, respectively. Monolithic TiN was grown at $V_s = 30$ V.

extent and approaches that of monolithic SiN_x. The monolithic single-crystal TiN film reached a hardness of 20.2 ± 0.9 GPa, which is in accordance with previous studies (20.3 ± 0.8 GPa).¹¹

Similar to earlier results,²⁵ the load–displacement curves indicate a higher elastic recovery for multilayer films compared to the TiN monoliths; e.g., for a 5-mN load, the monolithic TiN film exhibited an elastic recovery of ~33% whereas the corresponding values for multilayer films and monolithic SiN_x are higher, 50–60%. As can be seen in Fig. 8(b), bias affects the hardness quite substantially. With floating potential (approximately –17 V) during SiN_x deposition the multilayer is only

slightly harder than the monolithic TiN film grown at –30 V. Clearly, an increase in bias causes an increase in hardness, reaching a maximum of 37.6 ± 2.1 GPa at –60 V. In addition, changing the TiN layer thickness while maintaining the other parameters constant (5-Å SiN, 500 °C, and –30 V bias) made further tuning of the hardness possible. This resulted in a maximum hardness of 40.4 ± 0.8 GPa for 20 Å TiN layers [Fig. 8(b)]. For 5-Å TiN, the hardness drops but is still well above the value for monolithic TiN film. Hardnesses in films grown with 40 Å TiN and 5 Å SiN_x show similar hardness values when grown at 300 and 500 °C and at 32.1 ± 3.4 and 31.8 ± 1.0 GPa, respectively. Increasing the deposition temperature to 700 °C results in an increase in hardness to 38.1 ± 3.0 GPa.

IV. DISCUSSION

The finding of this study offers new insights to the nature of TiN/SiN_x interfaces. Based on the XRR and XRD results, TiN/SiN_x multilayer and TiN/SiN_x(001) superlattice films are shown to have well-defined interfaces and layers. In the multilayers are polycrystalline TiN and a-SiN_x ($x \geq 1$) layers. In the superlattices, TiN and SiN layers are both stoichiometric and epitaxial. The reflectivity curves from layered films, of which one example is shown in Fig. 1, exhibit sharp reflectivity peaks with additional Kiessig fringes, suggesting flat and sharp interfaces, which is expected when the strong segregation tendency between TiN and SiN_x is considered.^{26,27} In addition, the surface roughness can be maintained relatively low by using a low bias and well-polished substrates. The XRR simulations support this, suggesting an interfacial width in the low-ångström range.

The evidence for a strong compositional modulation within the films up to a SiN layer thickness of 6.8 Å is apparent in Fig. 2, where the diffractograms display SL peaks and additional Pendellösung fringes between SL peaks and Bragg peaks. Due to the template layer, the resulting fringe pattern is complex for small SiN layer thicknesses due to superpositioning of interference from the superlattice and template layer. However, with increasing SiN_x layer thickness, the fringes get better defined, which is clearly seen by comparing, for example, the multilayers with 3.5- and 13-Å SiN_x. The explanation for this behavior, and also for the loss of SL peaks for multilayers containing 10- to 13-Å SiN_x, lies in the formation of a-SiN_x. This formation is not occurring homogeneously along the entire surface [see Figs. 5(b) and 6(a)], but instead, a more plausible development is that a-SiN_x forms locally on the growing c-SiN layer surface during deposition as the layer thickness is increased. The parallel growth of a polycrystalline and epitaxial TiN on a-SiN_x and c-SiN, respectively, evolve rougher interfaces [Fig. 5(b)] compared to the case with a completely epitaxial film. This prevents constructive interference,

leading to the loss of the SL peaks and consequently Pendellösung fringes associated with the superlattice. However, the template layer is always the same, 500 Å of epitaxial TiN. Here, interference between the multilayer (SL)/template layer interface and the template layer/substrate interface cause fringes to appear in the diffractogram. This is also supported by a direct calculation of the thickness responsible for the interference fringes with a separation of $\Delta 2\theta$ (Fig. 2) using Eq. (1),

$$D = \frac{(m - n)\lambda}{2(\sin \theta_m - \sin \theta_n)} \quad (1)$$

where D equals the unknown thickness of the structure responsible for the measured fringes, θ_m and θ_n are the angular position for fringe m and n , respectively, and $\lambda = 1.54056$ Å. A calculation of D for the different samples in Fig. 2 results in 500 Å, i.e., the template layers' thickness. Hence, Pendellösung fringes originate from interference events within the films due to the high crystal quality of the superlattices and template layers. These types of fringes are only observed from layers with very high crystal quality, such as non-relaxed semiconductor epilayers, e.g., $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$, $\text{Ge}_{1-y}\text{C}_y/\text{Ge}_{1-x-y}\text{Si}_x\text{C}_y$, Mn/GaAs , and MnGa/GaAs .^{28–30}

The high crystal quality indicated by XRR and XRD is confirmed by RSM (Fig. 4) and (S)TEM [Figs. 5(a) and 6(a)], where the RSMs display SL peaks and extra Pendellösung fringes, and in the STEM [Fig. 6(b)], the stabilization of c-SiN is evident. No signs of any polycrystalline growth are observed as long as the SiN thickness is kept around this thickness (5.5 Å) or lower. The observed c-SiN lattice matches the TiN lattice well [Figs. 5(a) and 6(b)]. This agrees with recent density-functional theory calculations on NaCl structure SiN and TiN revealing lattice parameters for NaCl–SiN and NaCl–TiN equal to $0.99a_0$ and $0.986a_0$, respectively,^{2,27} where a_0 is a TiN lattice parameter.¹⁰ This difference in lattice parameter between the two phases is sufficient to be detected with XRD; however, no SiN peaks are observed, suggesting that the two phases are coherently strained to each other. Specifically, the small shift of the TiN 002 peak toward higher 2θ angles for samples containing 2.6- to 5.5-Å SiN (see Fig. 2) is indicative of a strain within the films, yielding an average superlattice 002 plane spacing that is smaller than that of pure TiN. This strain has likely additional sources, including thermal mismatch between film and substrate, thermal mismatch between the interlayers within the film, and point defects generated in the collision cascade during growth. It is apparent that the coherency strain contribution is the dominant one since the HRXRD peak shift disappears with the loss of epitaxial growth at ~7- to 13-Å SiN_x.

As discussed by Söderberg et al.,² the stabilization of metastable c-SiN can be attributed to pseudomorphic

forces, i.e., a minimization of the systems' interfacial energy by the formation of a coherent interface and lowering of the strain energy during nucleation and coalescence. As the metastable layer grows thicker, the elastic strain energy and molar enthalpy increase until the crystalline growth breaks down by a-SiN_x formation. For this process, it was further argued⁴ that a transition in bonding coordination in SiN_x from 6- to 4-folded follows, i.e., from octahedral to tetrahedral. Thus, the N content (x) should increase from $x \approx 1$ toward 1.33 (compare Si₃N₄). The ERDA results in Fig. 7 and Table II support an increase of N content as a-SiN_x forms. These two effects are responsible for the rapid transition to the amorphous phase, compared to epitaxial stabilization in other metastable material systems, e.g., AlN, where the stoichiometry remains constant.³¹

The multilayers show the highest hardness for thinner SiN_x layer thicknesses, Fig. 8(a). Within a single-crystal film, no grain boundaries exist that can act as dislocation obstacles. Instead, dislocation hindrance is obtained through Koehler hardening³² and from coherency strains due to the strained epitaxial SiN(001) interlayers. The grain boundaries formed in polycrystalline films with columnar epitaxial layer growth^{1,2} provides additional dislocation obstruction. On the other hand, it has been shown that columnar grain boundaries are sites where a material tends to shear and glide during deformation.^{16,33,34} The highest hardness observed in Fig. 8(a) for a film grown on MgO is ~7-Å SiN, to be compared to the polycrystalline case where reported highest hardness values are around 3- to 7-Å SiN_x.^{1,3,5} An explanation for the high value in this work is the fact that a single-crystal TiN template layer does not have any surface cusps at the emerging grain or column boundaries (see Fig. 7 in Ref. 1). Such cusps would cause the subsequent SiN layer to grow unevenly and possibly also act as a preferential site for amorphous tissue formation. Hence, with a single-crystal template, the growth front should be more flat and thereby provide the possibility to stabilize the thickest c-SiN layers.

By changing bias and/or temperature, the mobility of the arriving species can be affected. With a higher mobility, lower-energy positions should be easier to reach, acting favorably on the lattice and interfacial structure. This is seen for the 40-Å TiN, 5-Å SiN multilayer deposited at 500 °C, where the diffractogram exhibits clear Pendellösung fringes. For $T_s = 300$ °C, however, only SL peaks are observed (see Fig. 3). Hence, a higher temperature promotes higher-quality interfaces. At even higher temperature, $T_s = 700$ °C, we observe a higher degree of a-SiN_x which indicates that c-SiN is less stable at higher temperatures. Apparently, this mixture of a-SiN_x and c-SiN is beneficial from a mechanical properties point of view because an increase in hardness compared to the films grown at lower temperatures is

observed. Increasing the bias affects the hardness [Fig. 8(b)] through defect generation. When increasing the bias from floating potential to $V_s = 50\text{--}60\text{ V}$, the amount of point defects introduced in the lattice through collision cascades will increase. This causes an increase in compressive stresses and, subsequently, in hardness. Increasing the bias to $V_s = 50\text{--}60\text{ V}$ also causes a slight degradation of the SL peaks and fringes in the corresponding diffractogram, suggesting a degradation of the interfaces compared to the -30-V case. Hence, an intermediate bias should be used to achieve the highest crystal quality.

Decreasing the TiN layer thickness while maintaining the SiN_x layer thickness constant will further decrease the amount of space dislocation that can be used for propagation before an interface is approached. Thus the superlattice hardening is affected³² as plastic flow is effectively hindered through differences in elastic modulus, coherency strains, and Hall–Petch effects. This results in a $\sim 100\%$ hardness increase for samples with $20\text{-}\text{\AA}$ TiN compared to monolithic TiN films.

V. CONCLUSIONS

Multilayer films of transitional metal nitride TiN and covalently bonded SiN_x have been grown by codeposition of Ti and Si in an Ar/N_2 atmosphere. We present evidence for growth of high crystalline order single-crystal TiN/SiN(001) superlattice films exhibiting high film uniformity, similar to what is usually observed in semiconductor related films. Through high-resolution TEM and Z-contrast STEM, a direct view of the stabilized layers is provided. The epitaxial nature is lost as growth of $\alpha\text{-SiN}_x$ ($x \geq 1$) is initiated. However, as shown through STEM, even for a SiN_x layer thickness of $13\text{ \AA}$, the initial atomic layers grow epitaxially. With formation of $\alpha\text{-SiN}_x$, the N content in the coating increases as shown by ERDA. Also, the films grown are pure to the detection limit, with essentially no O present. The highest hardness values are observed within films exhibiting epitaxial SiN interlayers, but polycrystalline films also exhibit a higher hardness than do monolithic TiN and SiN_x films. Suggested hardening effects are Koehler hardening, coherency strains, and small crystallite sizes (when polycrystalline).

The Ti–Si–N system exhibits strong segregation between the constituent phases. Consequently, the binary compounds of this system have been targeted for the growth of super or potentially ultrahard nanocomposites.^{6–8} The three-dimensional geometry of grains and tissue phases in these nanocomposites makes the microstructural observation, e.g., through TEM, challenging. In this study, through use of multilayers as a model system, not only can the interfacial thickness be precisely controlled, but the two-dimensional structure also allows

for direct structural observation through TEM. The recent results presented herein and in Hultman et al.⁴ will have impacts on the interpretation of TiN– SiN_x nanocomposites as the presence of $\alpha\text{-SiN}$ or any other strain-stabilized SiN_x polytype depending on the given TiN surface must be taken into consideration.

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