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Self-organization during growth of ZrN/SiN_x multilayers by epitaxial lateral overgrowth

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ZrN/SiN_x nanoscale multilayers were deposited on ZrN seed layers grown on top of MgO(001) substrates by dc magnetron sputtering with a constant ZrN thickness of 40 Å and with an intended SiN_x thickness of 2, 4, 6, 8, and 15 Å at a substrate temperature of 800 °C and 6 Å at 500 °C. The films were investigated by X-ray diffraction, high-resolution scanning transmission electron microscopy, and energy dispersive X-ray spectroscopy. The investigations show that the SiN_x is amorphous and that the ZrN layers are crystalline. Growth of epitaxial cubic SiN_x—known to take place on TiN(001)—on ZrN(001) is excluded to the monolayer resolution of this study. During the course of SiN_x deposition, the material segregates to form surface precipitates in discontinuous layers for SiN_x thicknesses ≤ 6 Å that coalesce into continuous layers for 8 and 15 Å thickness at 800 °C, and for 6 Å at 500 °C. The SiN_x precipitates are aligned vertically. The ZrN layers in turn grow by epitaxial lateral overgrowth on the discontinuous SiN_x in samples deposited at 800 °C with up to 6 Å thick SiN_x layers. Effectively a self-organized nanostructure can be grown consisting of strings of 1–3 nm large SiN_x precipitates along apparent column boundaries in the epitaxial ZrN. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4838495>]

INTRODUCTION

Transition metal nitrides (TmN) such as TiN have been employed as hard coatings for over four decades. Through the incorporation of additional elements, e.g., Si, the coatings properties are enhanced, including increased oxidation resistance and hardness.¹ Since the solubility of Si is low or negligible in all TmN, the alloying during vapor-phase deposition often brings Tm-Si-N films into a nanocomposite state, consisting of nanocrystalline (nc-)TmN particles embedded in an amorphous SiN_x matrix.¹ For e.g., in Ti-, W-, and V-based systems, a matrix comprising tissue phases of SiN_x up to a few monolayers (ML) in thickness is coupled to increasing hardness.^{1,2}

Another way to enhance the properties by mixing different phases is to produce a nanoscale multilayer by sequential layer deposition, which can be seen as a two-dimensional representation of a nanocomposite. In a similar manner to composites, multilayers gain for instance mechanical properties (e.g., improved hardness³), optical properties (e.g., spectral selectivity⁴), and chemical properties (e.g., oxidation resistance⁵). In a multilayer, the layers corresponding to matrix and particles are aligned as a periodic structure in the growth direction. As such, the multilayer benefits interface and structure studies through cross-sectional investigations by, e.g., transmission electron microscopy (TEM). Such multilayer studies were carried out by Söderberg *et al.* on TiN/SiN_x where it was found that thin SiN_x layers can assume a cubic phase, epitaxially stabilized by the adjacent

TiN layers³ and, similar to Ti-Si-N nanocomposites, show an improved hardness (≥ 30 GPa)⁶ compared to films of its binary constituents (~ 20 GPa for TiN and ~ 25 GPa for SiN).⁷

Initial studies indicated similar properties between the Ti-Si-N and Zr-Si-N thin film system⁸ in terms of increased hardness compared to Ti-N and Zr-N, respectively.

Not only adding an element to the TmN system, but also replacing one of the Tm's brings the possibility to tweak the properties of a material as, e.g., in the case of amorphous ternary nitrides where the thermal stability is increased when comparing a-Ti-Si-N to a-Zr-Si-N.^{9,10} Therefore, in an analogous manner to the TiN/SiN_x multilayer investigations by Söderberg *et al.*, ZrN/SiN_x multilayers should be explored. Such multilayers were studied by Dong *et al.* using TEM and they found epitaxy through several periods for 6 Å SiN_x layers and a similar hardness to TiN/SiN_x.¹¹ However, when comparing Zr-Si-N films with Ti-Si-N films it has been found not only that the hardest films have different texture (columnar structure^{12,13} and nanocomposite,¹⁴ respectively), different decomposition mechanisms,¹⁵ but also different hardness dependence of silicon content (maximum hardness at ~ 3 at. % Si (Refs. 12 and 16) for Zr-Si-N and at ~ 5 –10 at. % Si for Ti-Si-N (Refs. 1 and 14)). In addition, different lattice parameters ($a_0 = 4.58$ Å for ZrN (Ref. 17) and $a_0 = 4.24$ Å for TiN (Ref. 18)), typically affect the structure of subsequently grown layers and the coherency at the interface.¹⁹ Therefore, further investigations are required to understand the growth of SiN_x, especially at the interface in TmN nanocomposites and multilayers.

In this paper, we systematically study the growth of ZrN/SiN_x multilayers deposited with varying SiN_x thickness and at different temperatures. We investigate the organization

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of SiN_x layers and the ZrN/SiN_x interfaces by high resolution scanning TEM (HR(S)TEM).

EXPERIMENTAL DETAILS

The multilayers were deposited in a high vacuum, dual cathode, dc reactive unbalanced magnetron sputtering system with base pressure $<3 \times 10^{-7}$ Torr. The deposition system is described in detail elsewhere.²⁰ The sputtering was carried out in an Ar (4 mTorr, 99.9997% pure)/N₂ (0.5 mTorr, 99.999% pure) atmosphere with 75 mm diameter, 3 mm thick water cooled targets, one zirconium (99.9%), and one silicon (99.999%) with a metal shield between the targets to prevent cross-contamination. With a constant target power of 200 W for the Zr target and 100 W for the Si target, using power regulation of each magnetron discharge, deposition rates of $r_{\text{Zr}} = 0.127$ nm/s and $r_{\text{Si}} = 0.146$ nm/s were obtained and the layer thicknesses were adjusted by two computer-controlled shutters located between the targets and the rotating substrate table. The substrates used for all samples were 10×10 mm² polished MgO(001), which were ultrasonically cleaned with trichloroethylene, acetone, and 2-propanol. Prior to deposition the substrates were degassed at 900 °C for ~1 h and then cooled to the deposition temperature.

The multilayers were deposited on the MgO(001) substrates after an initial deposition of a 50 nm seed layer of ZrN. The different samples were grown with identical number of periods ($N = 30$) and identical ZrN-layer thickness (40 Å), while the deposition time of the SiN_x was varied to correspond to a desired layer thickness of 2, 4, 6, 8, and 15 Å, respectively. For all samples, except one, the substrate holder was held at 800 °C, while for one of the 6 Å SiN_x layer samples the temperature was instead held at 500 °C during the deposition. The deposition conditions for all samples are summarized in Table I.

For deposition-rate determination and structural characterization of the multilayers hard X-ray (Cu-K_α) reflectivity (HXR) profiles were obtained using a Philips X'pert MRD.

Cross-sectional samples for scanning TEM ((S)TEM) studies were prepared by traditional cutting, gluing, and mechanical polishing followed by low angle Ar ion milling at 5 keV with a final fine polishing step at 1 keV.

High angle annular dark field (HAADF)-(S)TEM micrographs were obtained using the Linköping double corrected FEI Titan³ 60–300 operated at 300 kV, while the energy-dispersive X-ray ((S)TEM-EDX) spectroscopy maps were acquired with the embedded Super-X system.

TABLE I. Samples and deposition conditions.

Sample	No. of periods	ZrN thickness (Å)	SiN _x thickness (Å)	Deposition temperature (°C)
1	30	40	2	800
2	30	40	4	800
3	30	40	8	800
4	30	40	15	800
5	30	40	6	800
6	30	40	6	500

RESULTS

Figure 1 shows the XRD θ - 2θ scan from all six samples. It can be seen that the most apparent film peak is the ZrN(001) at 39.3°, epitaxially grown on the MgO(001) substrate (at 42.9°). For the samples grown at 800 °C with a desired SiN_x thickness of 4 Å superlattice (SL) reflections appear at 36.8° and for 6 Å at 37.0° and 34.8°, where the most prominent SL reflections are for the 6 Å sample.

In Figure 2 low-magnification cross-sectional HAADF-(S)TEM micrographs of the multilayer samples grown at 800 °C with SiN_x thicknesses of (a) 2 Å, (b) 4 Å, (c) 8 Å, and (d) 15 Å are shown for an overview. It can be seen that the two samples with SiN_x layers of 2 Å and 4 Å (Figures 2(a) and 2(b)), both show a weakly undulating contrast in the growth direction owing to the alternating ZrN and SiN_x depositions. For these two samples, an apparent columnar structure exhibiting diffraction contrast, which originates from the seed layer, extends through the entire film.

For the samples exhibiting the thicker SiN_x layers (8 Å and 15 Å), the contrast between the ZrN and SiN_x layers increases and grain boundaries only locally extend into the first few periods or across a few layers at random.

Figure 3 shows low-magnification cross-sectional HAADF-(S)TEM micrographs of the multilayer samples grown with a SiN_x thickness of 6 Å at 500 °C and 800 °C. These samples were chosen for further investigations as they exhibit a SiN_x layer thickness, which positions the multilayer in a transition from continuous epitaxial to polycrystalline multilayer with continuous ZrN and SiN_x layers. The sample grown at 500 °C (Figure 3(a)) exhibits little contrast between layers and a generally distorted appearance. For the sample grown at 800 °C (Figure 3(b)), the contrast between the ZrN and SiN_x layers is more pronounced than at 500 °C. It is also more pronounced than compared to the 4 Å sample grown at

FIG. 1. θ - 2θ XRD scans of samples with intended SiN_x thickness of 2 Å, 4 Å, 6 Å, 8 Å, and 15 Å deposited at 800 °C and 6 Å deposited at 500 °C.

FIG. 2. Overview HAADF-(S)TEM micrographs of the samples with SiN_x thickness (a) 2 Å, (b) 4 Å, (c) 8 Å, and (d) 15 Å.

the same temperature, but epitaxy is still preserved locally, as seen by a columnar appearance, although not extending towards the surface throughout the complete length of the film.

More detailed images of the structure for all samples can be seen in the HR(S)TEM micrographs viewed along $\langle 001 \rangle$ in Figures 4 and 5. For the 2 Å sample (Figure 4(a)), the lateral multilayer structure is barely visible, but a crystal structure of cubic appearance is maintained through the image. However, dark columnar features are found interlaced in the film. Slightly more pronounced lateral layers are found in the 4 Å SiN_x layer sample (Figure 4(b)), but with an even more prominent columnar appearance and with diffuse pockets emerging from inside the columns. From the cross-sectional view along $\langle 110 \rangle$, it can be seen that $\text{ZrN}\{111\}$ facets confine the pockets. In Figure 4(c), showing the sample with 8 Å SiN_x layers, a more distinct and continuous multilayer structure appears. Here, the SiN_x layers exhibit no crystalline appearance and are therefore concluded to be amorphous. The ZrN layers on the other hand are polycrystalline and locally form bridges across the SiN_x , which causes a diffuse appearance of the SiN_x layer with embedded lattice fringes. The sample with a SiN_x thickness of 15 Å also assume polycrystalline ZrN layers, but exhibits a sharper interface from a

FIG. 4. HR-(S)TEM micrographs of the samples grown at 800 °C, with SiN_x thickness (a) 2 Å, (b) 4 Å, (c) 8 Å, and (d) 15 Å.

ZrN layer to a SiN_x layer in the growth direction, compared to the 8 Å sample. However, a gradient can be seen in the SiN_x layer of the 15 Å sample towards the subsequent ZrN layer.

Figure 5 shows the HR-(S)TEM micrographs of the films grown with 6 Å SiN_x at 500 °C and 800 °C. The sample deposited at 500 °C exhibits a multilayer structure, similar to those of 8 and 15 Å deposited at 800 °C, i.e., amorphous, continuous SiN_x layers with polycrystalline ZrN layers. However, the sample grown at 800 °C has an appearance similar to the 2 and 4 Å samples with epitaxial growth and columns of dark, diffuse pockets. A difference compared to the thinner SiN_x layer samples, however, is that the dark pockets further arrange a more pronounced laterally extended layer structure. The layering is also reflected in the XRD measurements where the 6 Å sample grown at 800 °C has more and stronger superlattice reflections compared to the 4 Å sample grown at the same temperature.

FIG. 3. Overview HAADF-(S)TEM of the samples with SiN_x thickness 6 Å deposited at (a) 500 °C and (b) 800 °C.

FIG. 5. HR-(S)TEM micrographs of the samples with SiN_x thickness 6 Å deposited at (a) 500 °C and (b) 800 °C.

In Figure 6, EDX mapping results from the 4 Å SiN_x layer sample are shown together with a corresponding HAADF-(S)TEM micrograph of the mapped area. Figures 6(b) and 6(c) displays the Si and Zr distributions, respectively, while Figure 6(d) is the interwoven image of Figures 6(b) and 6(c). Neither the Si nor the Zr maps indicate a significantly extended layer structure, consistent with the corresponding (S)TEM image in Figure 4. On the other hand it can be concluded that both Si and Zr have a complementary undulating organization both laterally as well as vertically. When comparing the EDX maps with the HAADF micrograph, it can be seen that the bright areas directly correspond to the Zr distribution, while the dark pockets correspond to Si-rich precipitates. As a consequence of the limited spatial and statistical accuracy of the EDX measurements, it cannot be excluded that some Si is dissolved in the ZrN.

DISCUSSION

An important outcome of the experiments is that the as-deposited ZrN/SiN_x multilayers exhibit clearly separated crystalline ZrN and amorphous SiN_x phases. An apparent columnar structure extends through the multilayers from the ZrN seed layer. It is noteworthy that the amorphous SiN_x layers are discontinuous for an intended SiN_x thicknesses less than 6 Å while above this they become laterally continuous. This growth behavior can be explained by the very limited solubility of Si in ZrN and the substantial surface mobility of Si adatoms, as the deposition temperature corresponds to ~65% of the melting temperature of Si (1680 K (Ref. 21)) and ~50% of the melting temperature of comparable Si₃N₄ (2170 K (Ref. 21)). Apparently, each successive ZrN grows epitaxially and form continuous layers as a replica of the underlying ZrN surface, as can be seen for the 2 Å and 4 Å samples (Figures 4(a) and 4(b)). This means that the ZrN grows around and above the SiN_x precipitates, as by epitaxial lateral overgrowth.²² We propose a growth scheme where some SiN_x adspecies diffuse on the ZrN surface and precipitate at grain boundaries and surface defects of the ZrN to reduce surface energy, while the remaining SiN_x stay unbound on the ZrN layer. As the following ZrN layer is deposited, the arriving atoms land on both the SiN_x precipitates and the previously deposited ZrN layer. From the mixed source of adatoms, both the ZrN and SiN_x domains grow, but since the source of ZrN is renewed, and the SiN_x source is eventually depleted, the ZrN laterally overgrows the SiN_x

precipitates. As the ZrN cover the SiN_x precipitates, the ZrN furthermore forms {111} facets as a way to reduce interfacial energy to the SiN_x, as seen in the HR(S)TEM image (Figure 4(b)).

When the amount of deposited SiN_x is increasing, the SiN_x pockets extend laterally, which can be seen for the sample with 6 Å SiN_x (see Figure 5(b)) and eventually form a complete layer before any ZrN is deposited, as for the samples with 8 Å and 15 Å SiN_x layers (Figures 4(c) and 4(d)). Since the laterally extended SiN_x layers are amorphous and the pseudomorphic forces do not extend across the several ML-thick SiN_x layer, the ZrN renucleates and becomes a polycrystalline layer.

For the sample with 6 Å SiN_x layers deposited at 500 °C, the structure differs from that of the sample deposited at 800 °C. Obviously, the surface atom mobility at 500 °C is lower and the results suggest that the reduced temperature lowers the diffusion length and pins the arriving Si atoms into less organized positions on the surface. This results in the formation of an extended amorphous layer. Hence, the following ZrN will behave as for the case of a multilayer with thick SiN_x layers and become polycrystalline.

It should be pointed out that in none of the investigated structures was the presence of epitaxially stabilized cubic SiN_x observed, at least to the high effective resolution of the present experiment (~1 ML), which contrasts previous reports on ZrN/SiN_x multilayer structures.¹¹ This is presumably because our experimental method of choice ((S)TEM) is beneficial in detecting mass differences such as that between Zr and Si and hence observing separation amongst these elements, which is further confirmed by the EDX chemical mapping. The results by Dong *et al.*,¹¹ which suggest an epitaxial ZrN/SiN_x film, may be explained from the interpretation of, e.g., Figure 5(b) and the differences in applied methods—uncorrected HRTEM and aberration corrected HAADF-(S)TEM. While uncorrected HRTEM does not produce strong elemental contrast and also delocalizes lattice fringes due to spherical aberration (C_s), SiN_x inclusions like those visualized in Figure 5(b) may easily be overlooked and the structure appears epitaxially stabilized due to the bridging ZrN and by the homogeneously distributed lattice fringes. Thus, we submit that the formation of crystalline SiN_x on ZrN layers under typical deposition conditions of physical vapor deposition remains to be proven. For TiN/SiN_x multilayer structures, on the other hand, it was found that SiN_x can be stabilized in a cubic lattice. This was described in the research by Söderberg *et al.*²³ where (S)TEM was used to identify the cubic structure of SiN_x at similar growth conditions to the present layers (5–6 Å SiN_x at 500 °C and 5–6 Å SiN_x at 700–800 °C). SiN_x is obviously challenging to stabilize in a cubic lattice²⁴ and therefore the lattice match between layers is critical. Since SiN_x layers are stabilized on TiN ($a_0 = 4.24$ Å (Ref. 18)), the lattice mismatch may be too large to enable stabilization on ZrN ($a_0 = 4.58$ Å (Ref. 17)), which has an 8% larger lattice parameter than TiN.

FIG. 6. HAADF-(S)TEM (a) and EDX maps of the sample with 4 Å SiN_x—single element Si in (b), Zr in (c), and Si and Zr interwoven in (d).

CONCLUSIONS

Crystalline-ZrN/amorphous-SiN_x multilayers were grown by dual magnetron sputtering.

While SiN_x segregates to form surface precipitates on the ZrN layers, the transition thickness to achieve continuous SiN_x layers decreases with decreasing temperature, which is associated with the surface mobility of the Si adatoms. Specifically, it requires less than ~500 °C at 6 Å SiN_x thickness to form continuous layers and more than 8 Å for 800 °C substrate temperature.

We also find that the ZrN layers exhibit epitaxial lateral overgrowth on top of the SiN_x precipitates. Interestingly, a self-organized layer structure forms with vertical strings of 1–3 nm large SiN_x precipitates in an otherwise single-crystal ZrN matrix (for nominal SiN_x layer thickness of ≤6 Å).

No crystalline SiN_x layers are formed due to the large lattice mismatch to ZrN.

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