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

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ZrN/SiNx 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 SiNx 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 SiNx is amorphous and that the ZrN layers are crystalline. Growth of epitaxial cubic SiNx—known to take place on TiN(001)—on ZrN(001) is excluded to the monolayer resolution of this study. During the course of SiNx deposition, the material segregates to form surface precipitates in discontinuous layers for SiNx 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 SiNx precipitates are aligned vertically. The ZrN layers in turn grow by epitaxial lateral overgrowth on the discontinuous SiNx in samples deposited at 800 °C with up to 6 Å thick SiNx layers. Effectively a self-organized nanostructure can be grown consisting of strings of 1–3 nm large SiNx 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 SiNx matrix.1 For e.g., in Ti-, W-, and V-based systems, a matrix comprising tissue phases of SiNx 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/SiNx where it was found that thin SiNx 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/SiNx multilayer investigations by Söderberg et al., ZrN/SiNx multilayers should be explored. Such multilayers were studied by Dong et al. using TEM and they found epitaxy through several periods for 6 Å SiNx layers and a similar hardness to TiN/SiNx.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 structure12,13 and nanocomposite,14 respectively), different decomposition mechanisms15 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 (a0 = 4.58 Å for ZrN (Ref. 17) and a0 = 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 SiNx, especially at the interface in relation to TmN nanocomposites and multilayers.

In this paper, we systematically study the growth of ZrN/SiNx multilayers deposited with varying SiNx thickness and at different temperatures. We investigate the organization...
of SiNx layers and the ZrN/SiNx 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. The sputtering was carried out in an Ar (4 mTorr, 99.9997% pure)/N$_2$ (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 $r_{Zr} = 0.127$ nm/s and $r_{Si} = 0.146$ 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 $10 \times 10$ mm$^2$ 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 SiNx 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 SiNx 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$_\alpha$) 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 Titan$^3$ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of periods</th>
<th>ZrN thickness (Å)</th>
<th>SiNx thickness (Å)</th>
<th>Deposition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>40</td>
<td>2</td>
<td>800</td>
</tr>
<tr>
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<td>800</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>40</td>
<td>6</td>
<td>500</td>
</tr>
</tbody>
</table>

RESULTS

Figure 1 shows the XRD $\theta$–$2\theta$ 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 SiNx 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 SiNx 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 SiNx 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 SiNx deposition. 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 SiNx layers (8 Å and 15 Å), the contrast between the ZrN and SiNx 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 SiNx thickness of 6 Å at 500°C and 800°C. These samples were chosen for further investigations as they exhibit a SiNx layer thickness, which positions the multilayer in a transition from continuous epitaxial to polycrystalline multilayer with continuous ZrN and SiNx 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 SiNx layers is more pronounced than at 500°C. It is also more pronounced than compared to the 4 Å sample grown at

FIG. 1. $\theta$–$2\theta$ XRD scans of samples with intended SiNx thickness of 2 Å, 4 Å, 6 Å, 8 Å, and 15 Å deposited at 800°C and 6 Å deposited at 500°C.
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 \(h001\) 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 SiNx 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 \(110\), it can be seen that ZrN(111) facets confine the pockets. In Figure 4(c), showing the sample with 8 Å SiNx layers, a more distinct and continuous multilayer structure appears. Here, the SiNx 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 SiNx, which causes a diffuse appearance of the SiNx layer with embedded lattice fringes. The sample with a SiNx thickness of 15 Å also assume polycrystalline ZrN layers, but exhibits a sharper interface from a ZrN layer to a SiNx layer in the growth direction, compared to the 8 Å sample. However, a gradient can be seen in the SiNx 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 SiNx 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 SiNx 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 SiNx 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.
In Figure 6, EDX mapping results from the 4 Å SiNₓ 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/SiNₓ multilayers exhibit clearly separated crystalline ZrN and amorphous SiNₓ phases. An apparent columnar structure extends through the multilayers from the ZrN seed layer. It is noteworthy that the amorphous SiNₓ layers are discontinuous for an intended SiNₓ 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 eventually depleted, the ZrN laterally overgrow the SiNx precipitates. As the ZrN cover the SiNₓ precipitates, the ZrN furthermore forms {111} facets as a way to reduce interfacial energy to the SiNₓ, as seen in the HR(S)TEM image (Figure 4(b)).

When the amount of deposited SiNₓ is increasing, the SiNₓ pockets extend laterally, which can be seen for the sample with 6 Å SiNₓ (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 SiNₓ layers (Figures 4(c) and 4(d)). Since the laterally extended SiNₓ layers are amorphous and the pseudomorphic forces do not extend across the several ML-thick SiNₓ layer, the ZrN renucleates and becomes a polycrystalline layer.

For the sample with 6 Å SiNₓ 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 SiNₓ layers and become polycrystalline.

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

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

While SiNx segregates to form surface precipitates on the ZrN layers, the transition thickness to achieve continuous SiNx 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 SiNx 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 SiNx precipitates. Interestingly, a self-organized layer structure forms with vertical strings of 1–3 nm large SiNx precipitates in an otherwise single-crystal ZrN matrix (for nominal SiNx layer thickness of ≤6 Å).

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

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