Growth of epitaxial CrN on MgO(001): Role of deposition angle on surface morphological evolution

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Abstract

CrN layers, 6 to 500 nm thick, were grown on MgO(001) at 600 °C by ultra-high-vacuum magnetron sputter deposition in pure N₂ discharges at 2.6 Pa. The deposition angle \( \alpha \) with respect to the surface normal was varied from 0° to 80° in order to directly probe the effect of atomic shadowing on the surface morphological evolution. Layers grown with \( \alpha = 0° \) are single crystals which develop a regular surface mound structure. At low layer thicknesses, \( t \leq 25 \text{ nm} \), the surface mounds grow primarily vertically, due to kinetic roughening, and form square-shapes with edges along low-energy \( b_{100} \) directions. Continued growth at \( t \geq 25 \text{ nm} \) is dominated by mound-competition and coalescence which leads to a self-similar growth mode with increases in both mound height and width. Layers deposited from oblique angles \( \alpha = 80° \) also nucleate as single crystals with a cube-on-cube epitaxial relationship with the substrate. However, rough surfaces with cauliflower-type morphologies cause the nucleation of misoriented CrN grains that develop into cone-shaped grains that protrude out of the epitaxial matrix to form triangular faceted surface mounds. Atomic shadowing exacerbates the growth rate of these misoriented grains, causing a dramatic increase in the root-mean-square surface roughness, which is \( \sim 16 \times \) higher for layers grown at \( \alpha = 80° \) than at \( \alpha = 0° \). The roughening follows a power-law with a roughening exponent \( \beta \) that increases from 0.37 ± 0.04 to 0.57 ± 0.15 as \( \alpha \) is increased from 0° to 80°. This increase is attributed to a transition from kinetic roughening to roughening caused by atomic shadowing effects.

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1. Introduction

Transition-metal (TM) nitrides are well known for their remarkable physical properties including high hardness and mechanical strength, chemical inertness, and high temperature stability. As a result, they are widely studied and have become technologically important for applications such as hard wear-resistant coatings, diffusion barriers, and optical coatings. CrN has gained considerable interest over the past several years due to its superior high-temperature oxidation resistance [1–3], considerably higher than that of TiN, the primary industrial TM-nitride hard-coating. CrN has also been shown to possess high wear [4,5] and corrosion resistance [6], to provide improved system adherence as an interfacial layer between diamond films and steel [7], and to offer potential for use in phase-shift masks for photolithography [8] and etch-resistant hardmasks for X-ray absorber patterning [9].

We have previously reported on the growth of epitaxial CrN layers and have determined fundamental physical properties including mechanical, electronic transport, and optical properties and their relation to the CrN band-structure [10,11]. These epitaxial CrN layers exhibit unique 1-nm-wide nanopipes [11] and nanostaircases [12,13] which are open pores that extend through the entire layer thickness. Such nanopipes are particularly promising for future use as channels in single-molecule chemistry, lab-on-a-chip applications, molecular sieving, and DNA sequencing. The nanopipe formation mechanism is unknown but is presumably related to a complex interplay of anisotropic surface diffusion processes and atomic shadowing from a periodic surface mound structure [11–17]. The present study shows that atomic shadowing has a dramatic effect on the surface morphological evolution of epitaxial CrN(001) layers and is therefore expected to be also critical to the formation of nanopipes in these layers.

In this article, we present the results of an investigation where we use a variable deposition angle to directly probe the effect of atomic shadowing on the surface morphological evolution of
CrN layers grown on MgO(001) by reactive ultra-high vacuum (UHV) sputter deposition at a temperature $T_s=600$ °C. The surfaces of layers grown from a normal angle $\alpha=0^\circ$ develop square shaped mounds with edges along (100), directions that grow both vertically and laterally with increasing layer thickness. In contrast, the surfaces of layers grown from an oblique angle of $\alpha=80^\circ$ exhibit rougher surfaces with cauliflower-type morphologies. In addition, these layers develop misoriented grains that protrude out of the surface and exhibit an exacerbated growth rate due to strong shadowing effects. We attribute the change in surface morphological evolution with deposition angle to a transition from kinetic roughening to a roughening that is dominated by atomic shadowing effects. This transition is accompanied by an increase in the roughening exponent from 0.37 to 0.57.

2. Experimental procedure

All CrN$_x$ layers were grown in a loadlocked multi-chamber UHV stainless-steel dc magnetron sputter deposition system. The pressure in the sample introduction chamber was reduced to less than $1.3 \times 10^{-5}$ Pa ($1 \times 10^{-7}$ Torr), using a 60 l s$^{-1}$ turbomolecular pump (TMP), prior to initiating substrate exchange into the deposition chamber which has a base pressure of $1.3 \times 10^{-7}$ Pa ($1 \times 10^{-9}$ Torr), achieved using a 520 l s$^{-1}$ TMP. For deposition from a normal angle ($\alpha=0^\circ$), a water-cooled 7.5-cm-diameter Cr target with a purity of 99.95% was facing the substrate with a source-substrate-distance of 25 cm. For oblique angle deposition, the target was positioned at 10 cm from the substrate with the target center within the plane of the substrate surface. This arrangement yields a deposition flux which impinges at the substrate with an average azimuthal angle $\alpha$ of 80°, measured with respect to the sample normal. The angular distribution of the deposition flux, due to the finite size of the sputter source, was determined using the erosion-track on the target. It ranges from 77° to 90°, excluding the effects from vapor phase scattering.

The substrates were polished 10 $\times$ 10 $\times$ 0.5 mm$^3$ MgO(001) wafers cleaned with successive rinses in ultrasonic baths of trichloroethylene, acetone, methanol, and deionized water and blown dry with dry N$_2$. The wafers were then mounted on a molybdenum holder and inserted into the sample introduction chamber for transport to the growth chamber where they were thermally degassed at 800 °C for 1 h, a procedure shown to result in sharp MgO(001)1 $\times$ 1 reflection high-energy electron diffraction patterns [18]. 99.999% pure N$_2$ was further purified using a Micro Torr purifier and introduced through metering valves to reach a constant chamber pressure of 2.6 Pa (20 mTorr), which was measured using a capacitance manometer. Just prior to initiating deposition, the targets were sputter cleaned for 5 min while the substrate was covered with a protective disc. Sputtering was carried out at a constant power of 150 W, yielding deposition rates of 4.2 and 3.8 nm/min for $\alpha=0$ and 80°, respectively. The film growth temperature $T_s=600$ °C, including the contribution due to plasma heating, was measured with a pyrometer that was cross-calibrated by a thermocouple within the sample stage. The substrate was continuously rotated about the polar axis with 50 rpm, resulting in an overall circular symmetric deposition flux. Following deposition, the samples were allowed to cool to <50 °C before transferring them to the load lock chamber which was then vented with dry N$_2$.

The surface morphology of the films was investigated using tapping-mode atomic force microscopy (TMAFM) using a Digital Instruments Multimode SPM Nanoscope III with Nanodevices Tap300 silicon tips with tip radii of 10 nm. Linear planarized height profile images were obtained by removing sample tilt effects with standard software. The root-mean-square (rms) surface roughness and average mound heights and widths were determined from multiple micrographs.

Layer microstructures were analyzed by cross-sectional transmission electron microscopy (XTEM) using a Philips CM12 microscope with a LaB$_6$ filament operated at 120 kV. Cross-sectional specimens were prepared by first gluing two samples film-to-film with M-bond 610 and then cutting vertical sections with a wire saw. These sections were mechanically thinned with SiC to a specimen thickness of $\approx$30 μm. Final thinning to electron transparency was achieved by ion milling using a 5.0 kV Ar$^+$-ion beam incident at 12°.

3. Results and discussion

Fig. 1 are atomic force microscopy (AFM) images from CrN layers grown with a deposition flux that impinges normal ($\alpha=0^\circ$) to the substrate surface. The surface morphology from a 6.4-nm-thick layer, shown in Fig. 1(a), exhibits approximately circular surface mounds that have a density of 1400 μm$^{-2}$ and a distribution of widths, ranging from 12 to 30 nm, with an average width of 19 nm. The average rms surface roughness of 6.4-nm-thick layers is $0.27\pm 0.02$ nm. Fig. 1(b) shows an AFM micrograph from a layer grown under identical conditions as that shown in Fig. 1(a), but with a four times longer deposition time, that is, a 4× thicker layer than in Fig. 1(a), exhibits a smooth surface with a rms roughness of 0.44 $\pm$ 0.02 nm and exhibits mounds that tend to form squares with edges along (100), directions. The slight mound-elongation along the y-axis (also observed in Fig. 1(c)) is due to sample drift during imaging. The mound width ranges from 15 to 33 nm, with an average width of 23 nm. The image in Fig. 1(c) is from a layer which is another factor of 4 thicker than that in Fig. 1(b). The mounds have a density of 490 μm$^{-2}$ and their width ranges from 27 to 49 nm, with an average of 37 nm. The rms roughness of the 102-nm-thick layer is $0.75\pm 0.02$ nm.

We attribute the formation of surface mounds in epitaxial CrN(001) layers to kinetic roughening during deposition under conditions of low adatom mobility. The primary origin for kinetic roughening is the presence of Ehrlich–Schwoebel barriers [19], and/or deep traps at step edges [20], to the migration of adatoms over down-steps on growing surfaces. This leads to a divergence in adatom flux and, hence, increased nucleation on terraces which, in turn, gives rise to surface roughening and, with increasing film thickness, eventually even faceting. The lateral length scale is initially determined by the nucleation length for island formation. The islands and
resulting surface mounds form nearly circular shapes (Fig. 1(a)), since they are formed by surface diffusion kinetics which is isotropic on atomically flat CrN(001) surfaces. Continued layer growth causes then the mounds to increase in height, due to the asymmetric attachment at step edges, as discussed above. This vertical mound-growth is quantified by the measured rms surface roughness which increases by 60%, from 0.27 nm to 0.44 nm, when the layer grows from $t=6.4$ nm to $t=26$ nm. The lateral mound size is, in contrast, relatively little affected by this initial roughening. However, their lateral shape evolves from circular to square (compare Fig. 1(a) and (b)). This transition is not fully understood but is likely related to the interaction between neighboring mounds which causes edges to align along $\langle 100 \rangle$ directions. The $\langle 100 \rangle$ directions are the low-energy directions in cubic CrN, since they correspond to the primary bond directions between neighboring Cr and N atoms [10]. As the layer continues to grow, the surface morphological evolution is dominated by coalescence of surface mounds which causes smaller mounds to be incorporated into larger neighbors, which grow both vertically and laterally. This secondary growth mode is observed when comparing Fig. 1(b) and (c), (note the changing scale) for layers with $t=26$ and 102 nm, respectively. The vertical mound height increases, as determined by the rms surface roughness, by 70%, while the lateral mound width increases by 60%. The comparable growth rates indicate a self-similar growth mode where the aspect ratio of the surface mounds remains approximately constant.

Fig. 2(a) shows an atomic force microscopy (AFM) image of a 57-nm-thick CrN layer grown from an oblique angle $\alpha=80^\circ$. The most dominant features in the surface morphology are surface protrusions that appear as bright speckles in the micrograph. They have a density of 44 $\mu$m$^{-2}$ and their width, as determined by linear surface height profile analyses on 20 protrusions, ranges from 41 to 123 nm, with an average width of 73 nm. The corresponding height-range is 24 to 63 nm, with an average protrusion-height of 40 nm. The surface between the protrusions exhibits a mound structure with a root-mean square (rms) surface roughness of 2.3 nm. This value is considerably smaller than 8.6 nm, the rms-surface roughness of the entire surface, that is, including the surface protrusions. Fig. 2(b) is an AFM micrograph from a 230-nm-thick layer grown under identical conditions as the one shown in Fig. 2(a), but with a four times longer deposition time, that is, a four times larger layer thickness. The surface morphology is still dominated by surface protrusions, however, their density decreased by more than an order of magnitude, from 44 $\mu$m$^{-2}$ for $t=57$ nm to 3 $\mu$m$^{-2}$ for $t=230$ nm. They exhibit a triangular lateral shape, which is consistent with the XTEM analyses described below, showing that the protrusions are due to misoriented grains. The width and height of the protrusions

![Fig. 1. Tapping mode atomic force micrographs from CrN/MgO(001) layers deposited at 600 °C from a normal angle $\alpha=0^\circ$ with thicknesses (a) 6.4 nm, (b) 26 nm, and (c) 102 nm.](image1)

![Fig. 2. Atomic force micrographs from CrN/MgO(001) layers deposited from an oblique angle $\alpha=80^\circ$ with thicknesses (a) 57 nm and (b) 230 nm.](image2)
range from 249 to 359 nm and from 110 to 183 nm, respectively, with average width and height values of 281 and 138 nm, respectively. Comparing these values to those for the 57-nm-thick layer shows that the average width and height of surface protrusions increases by factors of 3.8 and 3.5, respectively, and the height-to-width aspect ratio remains nearly constant at ~0.5, when the layer thickness is increased by a factor of four. The surface between the protrusions, which constitutes ~85% of the overall surface, exhibits a mound structure with an rms-surface roughness of 3.0 nm. This portion of the surface resembles a cauliflower-type morphology which is common for deposition conditions where surface diffusion is negligible, that is, conditions where the incoming deposition flux is characterized by “hit-and-stick” [21]. However, the characteristic length scale of the surface mounds in the growth direction is approximately one order of magnitude smaller than that within the surface plane. Therefore, the resemblance of this surface to a cauliflower is somewhat artificial and caused by the exaggerated $z$-scale in the AFM image. The dark areas around the triangular surface protrusions in Fig. 2(b) indicate surface depressions caused by a reduced growth rate around surface protrusions due to atomic shadowing effects.

We attribute the decrease in number–density and the increase in size of the surface protrusions to a competitive growth mode. During growth, surface protrusions capture a larger fraction of the incoming deposition flux than the surrounding matrix, due to atomic shadowing effects that are particularly strong because of the purposely chosen oblique deposition angle of $80^\circ$. Consequently, their growth rate is exacerbated leading to a strong growth both in-plane as well as along the layer growth direction. However, if two or multiple protrusions are close together, as is the case for the surface shown in Fig. 2(a), atomic shadowing will favor the growth of one of these protrusions while the growth of the others is suppressed. This leads to a competitive growth mode where the larger protrusions grow at the expense of the smaller ones which die out.

Fig. 3(a) is a typical [100]-zone-axis cross-sectional transmission electron microscopy (XTEM) image with a corresponding selected area electron diffraction pattern (Fig. 3(b)) and a higher magnification micrograph (Fig. 3(c)), from a 500-nm-thick CrN/MgO(001) layer grown at $600 \, ^\circ\text{C}$ at an oblique deposition angle $\alpha=80^\circ$. The most prominent features in the XTEM micrograph are two cone-shaped grains that stick out of the surface. Electron diffraction analyses show that these grains are misoriented grains with the same cubic rocksalt crystal structure like the surrounding layer which is a single crystal CrN(001). The misoriented grains appear brighter than the surrounding matrix since their misorientation causes less electron scattering along the imaging direction which is aligned with the [100] direction of the MgO(001) substrate and CrN(001) layer. The micrograph shows an abrupt interface between the MgO(001) substrate and the CrN layer. The apparent decrease in layer thickness from the left to the right in the micrograph is due to the thinning process by ion-milling, which caused the top portion of the CrN layer on the right side to be milled away. There is some M-bond (used for XTEM sample preparation) observable on the layer on the left side of the image, indicating that the layer appears in the full size on this side, where it has a measured thickness of 475 nm, close to its nominal thickness of 500 nm, and a surface roughness with a peak-to-valley height of ~8 nm, in good agreement with the

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Fig. 3. (a) [100]-zone-axis cross-sectional transmission electron micrograph with (b) a corresponding selected area electron diffraction pattern and (c) a higher magnification micrograph of the area outlined in (a), from a 500-nm-thick CrN/MgO(001) layer grown at $600 \, ^\circ\text{C}$ at an oblique deposition angle $\alpha=80^\circ$. 
roughness observed by AFM. The 100 selected area diffraction pattern in Fig. 3(b), obtained with a 400-nm-aperture centered in the middle between the two misoriented grains, exhibits symmetric single-crystal reflections, some of which are indexed in the figure. These reflections do not change when the aperture is moved towards the substrate, indicating that the layer is a single-crystal with a cube-on-cube epitaxial relationship with the substrate: (001)\text{CrN}||(001)\text{MgO} with [100]\text{CrN}||[100]\text{MgO}. In addition, the SAED shows weak diffraction spots, as for example those indexed as 111 and 222 in Fig. 3(b). They are identified to arise from cubic CrN and only appear if the aperture includes one or multiple cone shaped grains, showing that these grains are misoriented CrN.

The XTEM analysis in Fig. 3 shows that the CrN layer deposited at $\alpha=80^\circ$ initially grows epitaxially until secondary nucleation leads to the formation of incommensurate misoriented CrN grains. The nucleation of these grains can be attributed to a combination of surface irregularities, such as cusps caused by the high roughness, and local surface regions stochastically encountering an insufficient N supply to sustain epitaxial growth, as previously reported for TaN [22]. The misoriented grains grow then in competition with the epitaxial region and form a cone shape. The (001) surface of CrN is expected to have the lowest surface energy, based on similarities to TiN [23]. Thus, misoriented grains, once nucleated, expose higher-energy surfaces to the growing flux and experience enhanced growth rates, as reported previously for TiN [24,25], Ti$_2$-N, AlN [26,27], ScN [28], and $\delta$-TaN [29] growth and in Monte Carlo simulations [30] of fcc film deposition. In each of these cases, the effect can be explained as being due to anisotropies in surface diffusivities and adatom potential energies [31]. That is, the average adatom residence time is significantly higher at lattice sites on low diffusivity (low potential energy) versus high diffusivity (high potential energy) surfaces. Thus, adatoms which are stochastically deposited near the grain boundary and, through surface diffusion, sample sites on both sides of the boundary between the epitaxial matrix and the misoriented grain, have a higher probability of finally being incorporated at the low-diffusivity surface which provides the more stable, lower potential energy sites.

Once a misoriented grain protrudes above the epitaxial CrN(001) layer, as shown in Fig. 3(c), its growth rate is further enhanced due to atomic shadowing resulting from the large average azimuthal deposition angle of $80^\circ$. The protruding grains collect a larger fraction of the incident deposition flux than the 001-oriented epitaxial region of the film. Thus, the misoriented grains grow faster than the surrounding matrix yielding surface protrusions, as observed in the AFM micrographs in Fig. 2. This growth mode also results in lateral growth which yields an increase in grain width as a function of layer thickness, as observed both in our AFM and XTEM analyses.

Fig. 4 is a plot of the rms surface roughness ($\sigma$) as a function of layer thickness, from CrN/MgO(001) layers comparable to those shown in Figs. 1 and 2. Each data point was obtained from analyses of multiple large (9 $\mu$m$^2$) micrographs. The plot includes layers grown with a deposition flux that is normal to the layer surface, $\alpha=0^\circ$, and layers with an oblique deposition angle $\alpha=80^\circ$. In addition, we also plot, $\sigma_{epi}$ the roughness of the epitaxial portion of layers grown with $\alpha=80^\circ$. These values exclude the contribution from surface protrusions that are due to misoriented grains, as observed in Figs. 2 and 3. The lines in Fig. 4 are obtained from fitting the measured data with a power law, $\sigma \propto t^\beta$, where $\beta$ is the roughening exponent.

The graph in Fig. 4 clearly shows that the surface roughness of layers grown from an oblique angle is considerably larger than if deposition impinges normal to the substrate surface. Comparing the roughness at $t=100$ nm indicates an increase in roughness by a factor of 16. In addition, the roughening rate, quantified by the exponent $\beta$, increases from $\beta=0.37\pm0.04$ to $0.57\pm0.15$. The roughness and roughening rate of the epitaxial portion of the 80$^\circ$-layer are $\sim 3 \times$ and $\sim 5 \times$ smaller than for the surface including protrusions, respectively. However, $\sigma_{epi}$ at $\alpha=80^\circ$ is still higher than $\sigma$ of the 0$^\circ$-layer. We attribute the dramatic increase in roughness with increasing $\alpha$ to atomic shadowing which becomes increasingly important as $\alpha$ increases. Atomic shadowing causes surface mounds to capture an over-proportional fraction of the incident deposition flux, leading to a higher growth rate of the mounds in comparison to the surface-valleys. This effect is most pronounced for the case where misoriented grains protrude out of the epitaxial matrix and have an exacerbated growth rate. However, even the epitaxial portion of the layer grown at $\alpha=80^\circ$ is considerably rougher than grown at $\alpha=0^\circ$. This roughness likely facilitates the nucleation of misoriented grains, since they are only observed for $\alpha=80^\circ$-layers. The measured roughening rate of $\sigma_{epi}$ is relatively low, $\beta=0.20\pm0.15$. This low rate is likely the result of misoriented grains, which are not accounted for when determining $\sigma_{epi}$, but which capture the fraction of the deposition flux that is most oblique. This causes the epitaxial portion of the surface to have a suppressed roughening rate as

![Fig. 4. Plot of the measured rms surface roughness ($\sigma$) as a function of layer thickness for normal ($\alpha=0^\circ$) and oblique ($\alpha=80^\circ$) deposition. $\sigma_{epi}$ is the surface roughness for $\alpha=80^\circ$ when excluding the misoriented-grain surface-protrusions in the analysis. The lines through the data are obtained from numerical fits using a power law, $\sigma \propto t^\beta$, where $\beta$ is the roughening exponent.](image-url)
soon as the shadowing from misoriented grains becomes dominant.

4. Conclusions

Atomic shadowing during deposition from oblique angles has a dramatic effect on the surface morphological evolution and, in turn, the microstructure of CrN layers grown on MgO(001). Kinetic roughening yields regular square-shaped surface mounds during deposition parallel to the surface normal. However, the surface forms a rough, cauliflower-type morphology during deposition from oblique angles. This rough surface causes the nucleation of misoriented grains that develop into surface protrusions that dramatically increase the rms surface roughness. The primary reason for the increased roughness is atomic shadowing which results in selective growth of surface mounds and protrusions at the expense of the surrounding matrix.

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