Unusual Magnesium Crystalline Nanoblades Grown by Oblique Angle Vapor Deposition

F. Tang∗, T. Parker, H.-F. Li, G.-C. Wang, and T.-M. Lu

Department of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, New York 12180-3590, USA

We observed the growth of unusual Mg nanoblades by oblique angle deposition. Although the vapor flux is obliquely incident, these nanoblades stand vertically on the substrates. The thickness of the Mg nanoblades along the incident vapor direction is reduced to ∼15 nm to ∼30 nm at a vapor incident angle ∼75°, while the width perpendicular to the incident vapor direction is as wide as a few hundred nm. In addition to the anisotropic blade morphology, a (1010) [0001] biaxial (II-O) texture was observed using in situ reflection high energy electron diffraction (RHEED). The tilt angles of the texture axis and the nanoblades are correlated with the high surface diffusion on the (0001) surface along the [2130] direction. We also propose that the observed very thin thickness of the nanoblade along the vapor flux direction is due to the appearance of the surface steps parallel to the [0110] direction and the low surface diffusion on the top surface of the nanoblades.

Keywords: Nanoblades, Oblique Angle Deposition, Shadowing Effect, Mg.

1. INTRODUCTION

Oblique angle deposition has been demonstrated to be an effective technique to produce three-dimensional nanostructures, such as nanospring and nanorods.1,2 In this technique, the vapor flux is incident at an oblique angle α with respect to the substrate normal while the substrate is stationary or rotating around the surface normal. As a result of the physical shadowing effect, the oblique incident vapor is preferentially deposited onto the highest surface features. This preferential growth dynamic gives rise to the formation of well-separated nanostructures. The dimension of these nanostructures typically ranges from tens to hundreds of nanometers, depending on the deposition material, deposition rate and the substrate temperature. For materials with high diffusivity the initial nucleation density is low and this can lead to more isolated structures. It is generally believed that in this case the dimensions of the deposited structures are larger. In addition to the shadowing effect and diffusion, the intrinsic microstructure of the deposited material also affects the formation of the nanostructures. For example, Wang et al. recently produced Y-shaped Cu nanorods induced by stacking faults during shadowing growth.3

In this paper, we report the growth of unusual Mg nanoblades by the oblique angle deposition with no substrate rotation. These nanoblades stand nearly vertically, violating the well-known tangent and cosine rules for columnar structures grown by oblique angle deposition.4,5 Our observations deviate from the traditional understanding of oblique angle deposition and require a new interpretation. The thickness of the Mg nanoblades along the incident vapor direction is ∼15 nm to ∼30 nm, while the width perpendicular to the incident vapor direction can be as wide as a few hundred nm. The formation of these extremely anisotropic structures with nanometer scale features shows that the growth of highly diffusive Mg deviates significantly from past experimental results and theoretical predictions.6–8 In addition to the anisotropic blade morphology, a biaxial (II-O) texture was observed using in situ reflection RHEED. The surface area to mass ratio reaches ∼52 m²/g using an average width of ∼22 nm. This value is about two orders of magnitude higher than that of ball-milled Mg powders that contain nano-crystallites.9 The nanoblades have potential applications in many areas due to this very high ratio. For example, the nanoblades could be used as a metal hydride for hydrogen storage or as a photocathode material.

2. EXPERIMENTAL DETAILS

In our experiment, an ultra high vacuum (UHV) thermal evaporation system was used to deposit the Mg nanoblades. The Mg pellets (purity 99.95%) were placed in an aluminum oxide crucible and heated resistively to the desired temperature of ∼653 K for evaporation. To study the effect of the vapor incidence angle, the deposition was performed simultaneously on four substrates mounted on a...
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3. RESULTS AND DATA ANALYSIS

3.1. SEM and TEM Images of the Nanoblades

Figures 1(a) to (d) and the insets show the SEM top view images of the deposited Mg films at different vapor incident angles. At normal vapor incidence, the film is continuous and is composed of polygon shaped crystals. The crystal sizes were on the order of a few micrometers. The measured angle between the edges of a crystal from the high-resolution SEM image shown in the top right inset of Figure 1(a) was around 125°. This suggests that these large crystals are the result of coalescence of multiple HCP (0001) oriented crystals. Taking the ratio of the substrate temperature to melting temperature of Mg yields a homologous temperature of ~0.34 (T_h = T/T_m = 310 K/923 K). This value of ~0.34 indicates that the growth of Mg should be in Zone II regime (0 < T_h < 0.5) according to the structural zone model of deposited films.\(^{10,11}\) The growth in Zone II regime implies a high atomic mobility, which is consistent with the large crystals observed in Figure 1(a). At a vapor incident angle of 30°, the film starts to form a stripe shaped structure perpendicular to the vapor incident direction, shown in Figure 1(b). The width of the stripe along the vapor incident direction is ~250 to 300 nm. As the deposition angle increases, the width of the stripes along the vapor incident direction dramatically decreases, forming thin nanoblades. At the vapor incident angle of 59°, the thickness of the nanoblades along the vapor incident direction varies from ~30 to 150 nm. Finally, at a vapor incident angle of 75°, the nanoblades become ultrathin with a thickness of ~15
to 30 nm. The width perpendicular to the vapor incident direction is on the order of a few hundred nm. A typical nanoblade is shown in the top right inset of Figure 1(d). We can clearly see surface steps along the width of the nanoblade.

Figure 2(a) shows the cross-sectional SEM image of the Mg film deposited at 75°. We can see that the nanoblades are almost vertical and run through the entire thickness of the film except near the substrate. In the early stage of growth (\( \sim 1 \mu m \)), some nanoblades obviously tilt away from the flux. The tilting angle of nanoblades is defined as \( \beta \), which is measured from the substrate normal as indicated in Figure 2(a). This tilting and vertical growth of the nanoblades violates the tangent and cosine rules that relate \( \beta \) to the incident flux angle \( \alpha \) during oblique angle deposition.\(^4\)

We plot the height of the film with respect to the vapor incident angle in Figure 2(b). Under our growth conditions the height along the substrate normal varies from a few \( \mu m \) to \( \sim 21 \mu m \) as the incident flux angle increases from 0° to 75°. We can see that the films deposited at the two highest incident vapor angles are much taller than the film deposited at normal vapor incidence, even though they received less flux. Previously it has been observed that films such as Co deposited at normal vapor incidence are thicker than films deposited at oblique angles.\(^5\) The disagreement comes from the vertically oriented nanoblades versus the conventional slanted nanorods grown by the oblique angle deposition. The unexpected height of the nanoblades is accompanied by the extremely porous nature of the film. In Figures 1(c) and (d) the nanoblades are separated from each other by \( \sim 1 \) to 2 \( \mu m \).

The single crystal nature of a single Mg nanoblade was investigated using TEM. Figure 3(a) shows the bright field TEM image of the Mg nanoblades that were deposited at to crystalline Mg was seen after the sample was exposed in the air.

![Fig. 2. Cross sectional SEM image of the Mg nanoblades deposited at a vapor incident angle \( \alpha \) of 75°. The black arrow indicates the tilted nanoblades at the beginning of the growth. Alpha (\( \alpha \)) and \( \beta \) are the vapor incident angle and the nanoblade tilting angle measured from the substrate normal, respectively. (b) A plot of the vertical heights of the nanoblade films as a function of the vapor incident angles.](image)

![Fig. 3. (a) TEM bright field image of the Mg nanoblades deposited at a vapor incident angle of 75°. The black arrow indicates the particular nanoblade that was selected for a detailed analysis. The inset of (a) shows one of the selective area electron diffraction (SAED) patterns of the nanoblade. In addition to the diffraction spots from crystalline Mg there is ring structure from MgO. (b) The lattice fringe image near the edge of the nanoblade. The interplanar distances for the (1210) plane and (1010) plane are measured to be 1.67 Å and 2.91 Å, respectively. About 2 to 4 nm thick oxidation region (MgO) adjacent to crystalline Mg was seen after the sample was exposed in the air.](image)
an incident vapor angle of ~75°. The black arrow indicates the nanoblade that was selected for a detailed analysis. One representative selective area electron diffraction (SAED) pattern along the (0001) zone axis is shown in the upper right inset of Figure 3(a). In addition to the spot pattern, two weak diffraction rings from polycrystalline MgO are labeled by white arrows in the diffraction pattern. The oxidation of the sample occurred after exposure to the air. Figure 3(b) is a HRTEM image taken near the edge of the nanoblade. The Mg lattice fringe is clearly seen in the image. The measured distances between lattice fringes in two orthogonal directions are ~2.91 Å and ~1.67 Å. These two values are close to the (10¯10) and (1210) interplanar distances of the Mg hexagonal close-packed (HCP) structure, which are 2.78 Å and 1.61 Å, respectively. We can also see from Figure 3(b) that an oxidation layer with the thickness of ~2 to ~4 nm is adjacent to the Mg crystal. The interface between Mg crystal and oxide is diffusive.

3.2. RHEED Patterns and Texture Analyses

In addition to the ex situ characterization of the Mg films, we used an in situ RHEED to study their crystalline orientations. From the SEM top view images of the nanoblades, we can see that they are well aligned, with the long sides approximately perpendicular to the vapor flux direction and the thin sides parallel to the vapor flux direction. This suggests that the Mg nanoblades also have two preferred crystalline orientations, namely biaxial or II-O texture. The biaxial texture is usually observed in the films grown by oblique angle deposition.13-15 Figures 4(a-d) show the in situ RHEED images of the Mg films deposited at different angles. The diffraction patterns of films grown at oblique angles were composed of distributed arcs that indicate a well-developed texture. As an example of the pattern analysis, we examine the diffraction pattern for α = 75°, shown in Figure 4(d). The ratios between the various radii of the diffraction arcs in Figure 4(d) are, 1:1.13:1.46:1.72:1.88. These ratios indicate that the diffraction arcs are from the (1010), (1011), (1012), (1120), and (1013) planes. The lattice constants a and c measured from the diffraction pattern are 3.18 ± 0.10 Å and 5.20 ± 0.17 Å. Both of the measured values are close to the values of Mg crystal, which are 3.21 and 5.21 Å, respectively. Through the analyses of the angles between different diffraction arcs,13 we found that the (1010) [0001] biaxial texture was formed in the Mg film. In this biaxial texture, the preferred orientations are the surface normal of the (1010) plane and the [0001] axis. The simulated diffraction pattern for this biaxial texture was superimposed on the top of the diffraction pattern in Figure 4(d). The (1010) texture axis, namely [2130] axis, is almost normal to the substrate, while the [0001] axis points along the vapor flux direction with an angle β = 85°. Beta prime (β′) is the tilting angle of the [0001] axis as measured from the substrate normal. This β′ angle (85°) suggests that the side faces of the nanoblades perpendicular to the flux direction are (0001) crystalline planes. Orthogonal to the [0001] and [2130] axes is the [0110] axis. Later in the discussion these three crystal axes will serve as a spatial reference. These axes are also indicated by the arrows shown in Figure 1(d). The β′ decreased to 79° and 45°.

Fig. 4. In situ RHEED images of the Mg films deposited at vapor incident angles of (a) 0°, (b) 30°, (c) 59°, and (d) 75°. The simulated diffraction pattern for a (1010) [0001] biaxial (II-O) texture was superimposed on the top of the measured diffraction pattern in Figure (d). Alpha (α) and β′ are the vapor incident and texture tilting angles measured from the substrate normal, respectively.
as the incident flux angle reduced from $\alpha = 59^\circ$ to $30^\circ$, respectively. At the normal vapor incidence, the diffraction patterns in Figure 4(a) showed a weak vertical (1011) fiber texture and an absence of (0001) planes parallel to the substrate.

4. DISCUSSION

From the RHEED analysis, we know that the side surface of the nanoblades that faces the flux is an (0001) plane. This plane is the most compact crystalline plane in the HCP structure, which has the lowest surface energy. Since the nanoblades stand vertically, the (0001) surface faces the vapor flux and consequently receives the majority of the flux. The formation of these long and thin nanoblades implies that the atoms deposited on the (0001) surface diffuse readily to the edges of this face and are transported to the adjacent surfaces, which are parallel to the vapor flux. The adjacent surfaces are higher surface energy planes such as (1010) planes, according to the equilibrium crystal structure. Additionally, in the SEM image in Figure 1(d), we observed the step structure on the crystal surface. These steps are more clearly seen in the initial growth of the crystal. Figure 5(a) shows a top view SEM image of a ~630 nm thick film, deposited at a vapor incident angle of 75°. In this image, a series of steps along the (0110) direction are clearly visible on the surface of the nanoblade, indicated by the black arrows. The step structure could indicate a high density of planer defects such as stacking faults parallel to the (0001) plane.18,19

4.1. Thin Thickness of the Nanoblades Along the Vapor Flux Direction

Based on the experimental observations, in Figure 5(b) a schematic of the proposed growth model is shown. After atoms land on the (0001) surface, they diffuse isotropically. This leads to the growth of the crystal along the [0110] and [2130] directions. The growth along the [0110] direction results in the disproportional width of the nanoblade in the direction perpendicular to the vapor flux. The growth along the [2130] direction contributes to the vertical growth of the nanoblades. As the atoms are transported to the adjacent (1010) surfaces the diffusion would be slower compared to that on the (0001) plane. This lower diffusion will lead to a reduced thickness of the nanoblades. However, the difference in the diffusion on these planes usually is small. Surface defects such as steps observed in the morphology of the nanoblades may be an important factor in accounting for the formation of the ultrathin thickness. Since the [1010] faces have a higher surface energy, the transported atoms will prefer to stay on these planes as shown in Figure 5(b). They may not have sufficient thermal energy to move over the nearby step onto the (0001) plane. Then the width of the step plateau along the [0001] axis, namely the vapor flux direction, will determine the width of the nanoblade in the flux direction. A systematic molecular dynamics (MD) simulation would be required to understand the detailed mechanism of the surface diffusion and the formation of the surface steps.

4.2. Tilting Angles of the Texture Axis and Nanoblades

The relationship between the tilting angle of the (0001) plane and the vapor incident angle can be understood using the van der Drift theory for highly diffusive surfaces.20 Base on this theory the nanoblades having the highest vertical growth rate will survive. For the nanoblade the vertical growth rate is a result of the diffusion along the [2130] direction. The total material received by the crystal is \( \sim \cos(\alpha - \beta') \), so that the growth rate \( V \) along the [2130] direction is also \( \sim \cos(\alpha - \beta') \). The vertical component \( V_z \) of the growth is \( \sim \cos(\alpha - \beta') \sin\beta' \). \( V_z \) is maximized when...
β′ = 45° + 1/2α. Using the values of α = 30°, 59°, and 75°, β′ is calculated to be 60°, 74.5° and 82.5°, respectively. We find that at high vapor incident angles α, i.e., 59°, and 75°, the predicted β′ values 74.5° and 82.5° are close to the experimental β′ values of 79° and 85°. However, for α = 30° the experimental β′ value is 45°, which is much smaller than the predicted value of 60°. This should be due to the reduced influence of the shadowing at smaller α angles. As the shadowing effect is weakened the crystals with smaller tilting angles are not suppressed. Since the nanoblades grow slowly along the [0001] axis, the growth along the [2130] axis causes the blades to tilt away from the flux at an angle β = 90° − β′, where β is measured from the substrate normal. The tall nanoblades that survived have large β′ values, meaning that those nanoblades stand nearly vertically. However, at the early stages of growth the nanoblades with a large tilting angle β, namely small β′, can also exist, as shown in the cross sectional SEM image in Figure 2(a). Markus Bauer et al. has observed that under oblique angle e-beam deposition, the MgO rods tilted slightly away from the vapor flux. They argued that this abnormal tilting angle is due to a directional diffusion originated from the momentum of the incident vapor atoms. In our experiments, for the 75° incident Mg flux it was close to a normal incidence on the (0001) surface of the nanoblades. In addition the kinetic energy of the Mg vapor atoms is very small at ~0.056 eV, so that directional diffusion should be negligible.

5. CONCLUSION

In summary, we studied the growth of the ultrathin Mg nanoblades by oblique angle deposition. These vertically-standing nanoblades possess a (1010) [0001] biaxial (H O) texture. We interpret both the tilt angles of the texturing axis and the nanoblades are due to the high surface diffusion on the (0001) surface. The very thin thickness of the nanoblade along the vapor flux direction is argued to relate to the surface steps and the low surface diffusion on the top surface of the nanoblades.

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References and Notes


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