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Structure zone model for extreme shadowing conditions

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ABSTRACT

Previously reported data on the microstructure of glancing angle deposited (GLAD) metal layers is used to extend the qualitative arguments of the structure zone model for physical vapor deposition to growth conditions with exacerbated atomic shadowing. At low growth temperatures T_s relative to the melting point T_m, the microstructural development is governed by atomic shadowing for both normal deposition and GLAD, resulting in fibrous grains with voided boundaries (Zone I). As the homologous growth temperature $\theta = T_s/T_m$ is raised above approximately 0.3, GLAD layers continue to exhibit well separated columns while conventional thin films show dense columnar microstructures (Zone II). $\theta > 0.5$ leads to equiaxed grains independent of deposition angle (Zone III). Therefore, strong shadowing during GLAD suppresses Zone II microstructures, causing a direct transition from Zone I to Zone III. GLAD microstructures can be divided into four distinct zones: *rods*, *columns*, *protrusions*, *and equiaxed grains*: separated self-affine *rods* form for $\theta < \theta_c = 0.24 \pm 0.2$, while considerably broader *columns* develop at $\theta > \theta_c$, due to exacerbated self-shadowing associated with an increased growth front roughness, causing larger growth exponents. Above $\theta \approx 0.35$, *protrusions* develop on top of some columns as they capture an overproportionate amount of deposition flux and grow much higher than the surrounding layer. At $\theta > 0.5$, diffusion processes dominate over atomic shadowing, leading to faceted rough layers with *equiaxed* grains. In addition, the large mass transport facilitates the formation of whiskers that form for many metal GLAD layers at $\theta > 0.4$.

1. Introduction

The microstructure of films deposited by physical vapor deposition (PVD) depends on the processing parameters such as substrate temperature T_s [1–5], gas pressure [1,4,6–9], ion bombardment [9–11], impurities [5], deposition geometry [11,12], substrate roughness [13] and substrate rotation [14]. The systematic analysis of the microstructure of films grown by a normal deposition flux led to the development of the structure zone model (SZM) [1,4,15,16], which qualitatively explains the morphology development as a function of adatom mobility controlled by the process parameters. The fundamental physical processes at play during growth are shadowing and surface diffusion [2]. Shadowing depends on the deposition angle and causes preferential deposition on mounds, leading to the formation of a rough, porous, columnar microstructure. On the other hand, diffusion leads to a reduction in porosity and a smoothening of the film surface. It is controlled by T_s, ion bombardment, impurities and the material system [1]. The initial SZM and the later revisions explain morphological changes in terms of the interplay between the competing phenomena of shadowing and diffusion, and classify the different film morphologies into zones (I, T, II and III) [1,4,5,15,16] as a function of increasing adatom mobility, while keeping the “degree” of shadowing constant.

In contrast, glancing angle deposition (GLAD) [17,18] is a PVD technique where the shadowing effect is purposely exacerbated by a grazing incident angle $\alpha > 80°$ of the deposition flux. This leads to the formation of self-affine [19] isolated columnar nanorod structures with a high level of porosity [20] and surface roughness [21] in a wide range of material systems [16,22] including metals [23] and covalently bonded materials [24]. Most research on GLAD is done at low temperatures, so that surface diffusion is kinetically limited and the dominance of atomic shadowing can be exploited to create arrays of nanostructures including straight and slanted pillars [18], springs [25], spirals [26], tubes [27] and branched [28,29] or multi-component nanorods [30,31]. The rod width w broadens with height h [28], which is attributed to growth competition [32,33] and is described by a power law scaling relationship [19,34]

$$w \propto h^p, \quad (1)$$

where p is the growth exponent [23,24,35,36] which depends on process parameters including the angle of incidence [21,23,37], the substrate rotation [38–40], substrate patterning [18,32,39,41,42], the material system under consideration [36] and T_s [43–45].

Recent studies on the microstructural evolution of GLAD layers at elevated temperatures [46–54] provide a motivation to revisit the fundamental competition between atomic shadowing and surface diffusion. The SZM cannot correctly describe GLAD microstructures because it assumes limited shadowing conditions which do not account for large deposition angles. Conversely, models that describe GLAD microstructural

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features including layer porosity [55,56] and column tilt [57,58] and broadening [19,34] assume negligible or limited surface diffusion and therefore do not account for temperatures that exceed ~1/3 of the melting point. The question arises regarding what layer microstructure is expected at both a high growth temperature and a large deposition angle, that is, for large surface diffusion *and* strong atomic shadowing.

In this article, we review recent experimental work on the temperature dependence of the microstructure of GLAD layers and discuss it within the framework of the SZM. For this purpose, the growth temperature is normalized by the melting point T_m of the deposited material, to yield the homologous growth temperature $\theta = T_s/T_m$. At low temperature, GLAD layers consist of high-aspect-ratio *rods*. Increasing θ leads to a continuous increase in their width. This is exacerbated by anomalous broadening at $\theta > \sim 0.24$, resulting in relatively broad *columns*. Growth competition at $\theta > \sim 0.35$ yields *protrusions* that extend above the surface of the surrounding film. At $\theta > \sim 0.5$, considerable mass transport results in approximately *equiaxed grains* and, for many metals, in the formation of *whiskers*. In contrast to the structure zone model for normal deposition, GLAD results in highly underdense microstructures up to $\theta \sim 0.5$. That is, there is a direct transition from a Zone I to a Zone III microstructure, while Zone II is suppressed due to the large shadowing length scale that limits the densification through surface diffusion for $\theta = 0.3$–0.5.

2. Experimental data

In this section, we summarize and discuss previously reported microstructural data of GLAD layers as a function of T_s. The temperature dependence of GLAD microstructures has only relatively recently gained interest. Thus, most data that is discussed in this section has been reported within the last five years and stems primarily from four different research groups, including our own. It includes GLAD layers deposited by sputtering and by evaporation from angles $\alpha \geq 80°$, with typically a continuously rotating substrate such that the net nanostructure growth direction is perpendicular to the substrate surface. The primary focus of this discussion is to understand the impact of increasing surface diffusion, facilitated by increasing θ, on the microstructural development of layers deposited by GLAD. Other deposition parameters, including the angular distribution of the deposition flux as well as growth rate and substrate rotation rate may also affect the microstructure but are, for clarity purposes, not discussed here. Instead, our particular interest is in temperature-induced qualitative changes in the microstructure which are observable for various material systems and scale with the homologous deposition temperature. They are all a direct result of the competition between atomic shadowing and surface diffusion.

High temperature GLAD was pioneered by Suzuki et al., [47,48] who reported Al layer microstructures which exhibit rough surfaces, approximately equiaxed grains, and whiskers. They attribute the microstructural evolution to diffusion at elevated temperatures [47] which suppresses the formation of separated columns typical for low-temperature GLAD. Similarly, the formation of whiskers is also facilitated by considerable diffusion [48], and is reported for various other metals including Cu, Ag, Au, Mn, Fe, Co, Ni and Zn deposited at 390 °C [49,50]. Comparing the reported micrographs for Al as a function of temperature indicates a transition from a microstructure that is dominated by separated columns at $T_s = 85$ °C to a continuous layer with whiskers at $T_s = 290$ °C [48]. This indicates a transition from a shadowing dominated to a diffusion-dominated microstructural development. At an intermediate temperature of $T_s = 180$ °C, Al layers are porous and exhibit a columnar microstructure. However, their surface is very rough and the columns are of irregular shape, with some columns extending well above the column tips of their neighbors [48], a microstructural feature that we refer to as *protrusions* [33]. These results are summarized in Fig. 1, which is a plot that includes the microstructural information from all temperature dependent GLAD data discussed in this section. For the case of aluminum deposited by Suzuki et al., the columns and protrusions at $T_s = 85$ and 180 °C are indicated by symbols "**c**" and "**p**" at $\theta = 0.38$ and 0.49, respectively, while $T_s \geq 290$ °C leads to dense layers with equiaxed grains and whiskers, indicated by overlaying symbols "**e**" and "**w**". Due to the relatively low melting point $T_m = 933$ K of Al, none of the reported Al GLAD microstructures is described as *rods* "**r**". The low-temperature rod-microstructure is characterized by vertical rods which are narrower and exhibit a smaller broadening rate than the columns. The transition from rods to columns is due to a transition from a 2D to a 3D island growth mode, as discussed in more detail below.

Suzuki et al. also reported the microstructure of Fe deposited by GLAD as a function of T_s [50]. They found conventional GLAD columns at $T_s \leq 300$ °C and irregular microstructures with protrusions for $T_s \geq 330$ °C. In addition, whiskers start to develop above 330 °C, indicating that surface diffusion is sufficient for whisker formation at 330 °C ($\theta = 0.33$), while the columnar microstructure with protrusions suggests that atomic shadowing dominates over surface diffusion in determining the overall microstructural development up to $\theta \sim 0.44$ for Fe [49,50], as indicated in Fig. 1 for the Fe melting point of 1811 K.

Deniz et al. [51] studied the microstructure of various metals and oxides deposited by GLAD as a function of T_s. They introduced the interesting concept of a threshold temperature Θ_T above which no nanostructuring occurs. The deposited layers are considered "nanostructured" if they consist of nanostructures that are separated by >2 nm and exhibit a height-to-width aspect ratio of ~10 or more. This is a good definition from a practical perspective, as it provides the useful temperature regime over which arrays of distinct GLAD nanostructure arrays can be deposited. In the context of the current discussion, microstructures characterized by *rods* or *columns* are considered to be "nanostructured", as they consist of well-separated structures that exhibit a large height-to-width aspect ratio. In contrast, protrusions and equiaxed grains do not satisfy the "nanostructuring" definition by Deniz et al., since the width of the *protrusions* can approach their height, and *equiaxed grains* have an aspect ratio of ~1 and also exhibit no gap between them. Thus, within the sequence of microstructures with increasing temperature from **r** to **c** to **p**

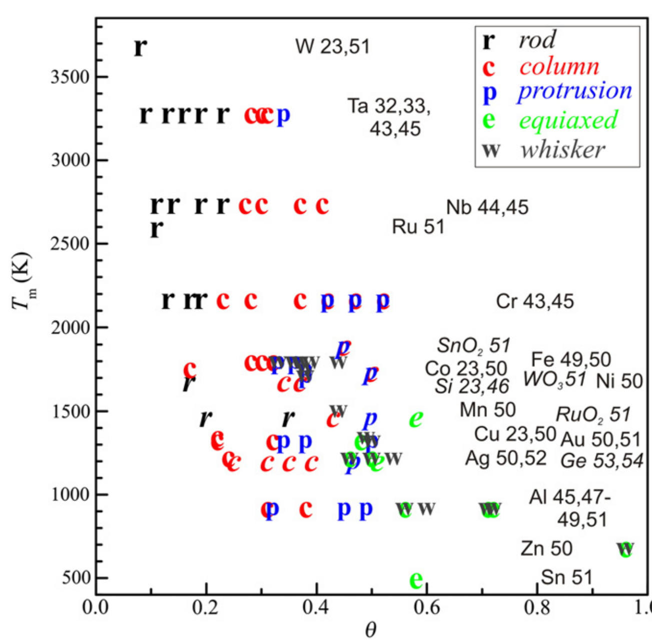

Fig. 1. High-temperature GLAD microstructural data from Refs. [23,32,33,43–54,59] for metallic and non-metallic systems classified into four zones: *rods* **r**, *columns* **c**, *protrusions* **p**, and *equiaxed* **e** grains. Microstructures that exhibit *whiskers* **w** are also labeled. The y-axis corresponds to the melting point T_m and the x-axis shows the homologous deposition temperature $\theta = T_s/T_m$. Each row of data points is labeled on the right, indicating the material as well as the relevant references. Italic symbols indicate non-metallic systems.