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Kinetics of a retracting solid film edge: The case of high surface anisotropy

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A model describing the retraction kinetics of a fully faceted edge of a single crystalline thin film deposited on a non-wetting substrate is proposed. The kinetics of retraction is very similar to that of a fully isotropic film. The calculated topography profile of the edge exhibits a single maximum and no local minima (depressions). The implications for the solid-state dewetting mechanisms are discussed.

Keywords: Thin films; Surface diffusion; Surface energy; Facets; Surface anisotropy

Solid-state dewetting or agglomeration of thin films is a process by which a thin continuous film uncovers a substrate and transforms into an ensemble of isolated particles. Dewetting is well known for thin metal films on ceramic substrates because the wettability of oxide ceramics by metals is poor and exposing the substrate reduces the total interfacial energy of the system [1–4]. According to a widely accepted point of view [5], the film dewetting in the solid state is controlled by the kinetics of a receding film edge, either circular [6] or planar [7]. The material of the film removed from the substrate accumulates close to the edge, forming a characteristic hill, provided that the material is transported by a diffusion mechanism and no material is lost due to evaporation. At larger distances from the film edge, the hill is followed by a depression [6]. Both the hill height and depression depth increase with increasing heat treatment time. Once the depression has reached the substrate, the hill pinches off from the rest of the film, forming an isolated island. Immediately thereafter the formation of a new hill begins in the remaining part of the film, renewing this mass-shedding process [7]. In the long run, because of the periodic mass shedding at the receding edge, the latter retracts with a constant speed over a long period of time [7].

Recent experimental data on agglomeration of thin solid films challenge the simplified dewetting scenario presented above. For example, the cross-sectional electron microscopy micrographs of receding edges of the 10–30 nm thick polycrystalline Au films deposited on oxidized Si substrates presented by Müller and Spolenak [4] clearly demonstrate a faceted nature of the hill and the absence of a nearby depression. Hill faceting and the lack of any depression are also obvious on cross-sectional micrographs and atomic force microscopy (AFM) topography images of the receding edges of single crystal Ni films deposited on MgO substrates [8], and of thin Si film on SiO_2 [9].

The faceted nature of the receding film edge poses a serious challenge to the theoretical description of the process kinetics. Indeed, the existing theories of the process are based on a classical picture of the curvature-driven surface diffusion (we assume that, for the very thin films considered in the present work, the contribution of surface diffusion to the mass transport dominates over that of bulk diffusion) [6,7]. This description fails for atomically flat facets which do not exhibit any mathematical curvature.

Carter et al. [10] proposed a general method for treating diffusion-controlled shape evolution of fully faceted crystals. In the present work, we will apply this method to the description of receding kinetics of the fully faceted thin film edge. Dornel et al. [9] developed a numerical algorithm for the description of anisotropic film edges that is based on the same ideas of thermodynamics of anisotropic surfaces used by Carter et al. [10]. It was shown that the depth of the depression close to the film edge strongly depends on the details of the γ-plot (the

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polar plot of surface energy vs. surface normal orientation). However, for the γ-plots investigated in the work of Dornel et al. both the flat facets and smoothly curved surfaces were present in the film edge profile [9]. The aim of this work is to investigate the effect of strong surface anisotropy on the shape evolution of film edges. Therefore, we will consider only fully faceted surfaces and adopt the approach of Carter et al. [10] for describing their kinetics.

Keeping in mind the applications to thin films of Au and Au-based alloys, we will consider the film edge defined by only two types of facets (Fig. 1). Indeed, only the {1 1 1} and {1 0 0} facets are present in the equilibrium shape of small Au single crystals [11], and in most cases as-deposited Au films exhibit a strong ⟨1 1 1⟩ texture [4]. The film edge retracts because the atoms from facets *ab* and *bc* move (by surface diffusion mechanism) to facets *cd* and *de* (the latter is parallel to *ab*). We also introduce an additional facet *ef* (parallel to *bc*), to check the possibility of the depression development behind the moving hill.

Following the approach of Ref. [10], the average chemical potential of the atom on the *n*th facet, μ_n, can be calculated as a variation of total surface energy of the system, E, with respect to the normal displacement of the facet, δn_n:

$$\mu_n = \Omega \frac{\delta E}{A_n \delta n_n} \tag{1}$$

Here A_n is the area of the facet, and Ω is the atomic volume. Applying Eq. (1) to the geometry of Figure 1 leads to the following expressions for the average chemical potentials of the atoms on the facets:

$$\mu_{ab} = \frac{\Omega}{h_1}\left[\gamma_i - \gamma_s + \frac{\gamma_{ab}\sin\varphi_2 + \gamma_{bc}\sin\varphi_1}{\sin(\varphi_1+\varphi_2)}\right] \tag{2a}$$

$$\mu_{bc} = \frac{\Omega}{h_2}\left[\gamma_{cd} + \frac{\gamma_{ab}\sin\varphi_2 + \gamma_{bc}\sin\varphi_1}{\sin(\varphi_1+\varphi_2)}\right] \tag{2b}$$

$$\mu_{cd} = \frac{\Omega}{w}\left[\frac{\gamma_{bc} - \gamma_{cd}\cos\varphi_2}{\sin\varphi_2} + \frac{\gamma_{ab} - \gamma_{cd}\cos\varphi_1}{\sin\varphi_1}\right] \tag{2c}$$

$$\mu_{de} = \frac{\Omega}{h_1+h_2+h_3-h_0}\left[\gamma_{cd} - \frac{\gamma_{ab}\sin\varphi_2 + \gamma_{bc}\sin\varphi_1}{\sin(\varphi_1+\varphi_2)}\right] \tag{2d}$$

$$\mu_{ef} = \frac{\Omega}{h_3}\left[\gamma_{cd} - \frac{\gamma_{ab}\sin\varphi_2 + \gamma_{bc}\sin\varphi_1}{\sin(\varphi_1+\varphi_2)}\right] \tag{2e}$$

where γ_i is the energy of film/substrate interface, and γ_{ab}, γ_{bc}, etc. denote the energies of the respective facets. The meaning of the geometrical parameters h_0, h_1, h_2, h_3, ϕ_1 and ϕ_2 is clear from Figure 1. In Eq. (2) we took into account the fact that the facet couples *de*–*ab*, *ef*–*bc* and *fg*–*cd* represent crystalographically identical surfaces and therefore $\gamma_{de} = \gamma_{ab}$, $\gamma_{ef} = \gamma_{bc}$ and $\gamma_{fg} = \gamma_{cd}$. It should be noted that the chemical potentials in Eq. (2) should be understood as excess quantities associated with the finite length of the facets, something which is similar to surface curvature in the thermodynamics of smoothly curved surfaces. In this respect, $\mu_{fg} = 0$, because the initial film is infinitely long.

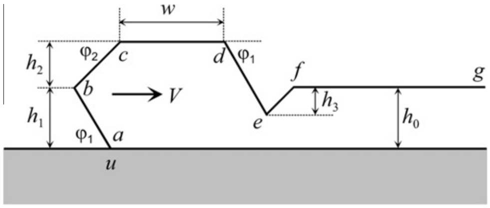

Figure 1. Anisotropic edge of a thin film with all geometric parameters of the model shown.

The normal velocity of the facet *xy*, V_{xy}, is determined by the difference of the incoming, J_x, and outgoing, J_y, surface diffusion fluxes:

$$V_{xy} = \Omega \frac{J_x - J_y}{l_{xy}} \tag{3}$$

where l_{xy} is the facet length. We calculate these fluxes using the approach of Ref. [10]. While the average values of chemical potential for the facets *xy*, μ_{xy}, are given by Eq. (2), the chemical potential itself is a function of the distance along the facet, *s*. To find this functional dependence, $\mu(s)$, we note that the surface diffusion flux, *J*, is proportional to the gradient of the chemical potential along the surface, while the normal velocity of the surface, *V*, is proportional to the divergence of this flux:

$$J = -\frac{D\nu}{kT}\frac{\partial\mu}{\partial s}; \quad V = -\Omega\frac{\partial J}{\partial s} \tag{4}$$

In these equations D and ν are the effective surface diffusion coefficient and the density of the mobile atoms per unit area of the surface, respectively, and kT has its usual thermodynamic meaning. The first expression in Eq. (4) is based on the Nernst–Einstein relation and is valid in the thermodynamic limit of a low driving force for diffusion. Martin and Benoist [12] demonstrated that significant differences of the diffusion concentration profiles calculated employing the atomistic jump frequency approach and the classical diffusion equation approach are observed for the width of the diffusion zone $X \leqslant 10a$, where a is the interplanar spacing of the crystal. Based on this result, the lower bound of the film thickness, h_0^*, for which the approach based on Eq. (4) is valid, can be estimated as $h_0^* = \sqrt{\frac{10\Omega\gamma_{cd}a}{kT}}$, which for the parameters for pure Au yields $h_0^* \approx 2\,\text{nm}$ (for $T = 500\,\text{K}$). Therefore, our model can be applied to films thicker than just few nanometers.

Because all points on the facet move simultaneously with identical velocities, the velocity V does not depend on s, hence $\mu(s)$ is a parabolic function of s. For the facet *xy*, this means:

$$J_{x+} = -\frac{\nu_{xy}D_{xy}}{kT}\left(\frac{\partial\mu}{\partial s}\right)_{x+} = -\frac{\nu_{xy}D_{xy}}{kT}\,\frac{6\mu_{xy} - 4\mu_x - 2\mu_y}{l_{xy}} \tag{5}$$

$$J_{y-} = -\frac{\nu_{xy}D_{xy}}{kT}\left(\frac{\partial\mu}{\partial x}\right)_{y-} = -\frac{\nu_{xy}D_{xy}}{kT}\,\frac{-6\mu_{xy} + 2\mu_x + 4\mu_y}{l_{xy}} \tag{6}$$

where μ_x and μ_y are the chemical potentials at the facet edges x and y, respectively. The normal velocity of the facet is then:

$$V_{xy} = -\Omega\frac{J_{y-} - J_{x+}}{l_{xy}} = 6\frac{\nu_{xy}D_{xy}\Omega}{l_{xy}^2 kT}(\mu_x + \mu_y - 2\mu_{xy}) \tag{7}$$

The unknown values of the chemical potentials μ_x, μ_y,… can be found from the conditions of continuity of the surface diffusion fluxes at the facet edges. This yields