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A liquid-like model for the morphology evolution of ion bombarded thin films

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ABSTRACT

Thin solid films exposed to ion irradiation exhibit a peculiar evolution that can differ substantially from what is observed for bulk samples. The phenomenology of the patterns that self-organize on the substrate is very rich, with morphologies that display several degrees of order upon the modification of initial film characteristics and irradiation parameters. This richness paves the way for the fabrication of novel functional surfaces, but it is also an indication of the complexity of the underlying driving mechanisms. A remarkable simplification for the comprehension of these phenomena can come from the noteworthy similarity of the obtained patterns with those showing up when liquids dewet from their substrates. Here, we analyze the possibility to apply a liquid-like model to explain the morphology evolution of ion bombarded thin films for the whole phenomenology showing up in experiments. In establishing this connection between liquids and ion bombarded thin films, we propose to use also for liquids the insight gained for our system with recent experiments that stress the importance of the substrate topography for the selection of the dewetting mechanism. If confirmed, this result would lead to a reconsideration of the importance of capillary waves in spinodal dewetting, and will help to understand the low reproducibility of the related experimental results.

1. Introduction

Ion irradiation of thin solid films can induce surface morphologies that differ substantially from the outcome observed in the case of bulk samples [1]. Common, peculiar patterns, where the substrate appears partially exposed, and the film materials thickens around holes or in labyrinth-like structures, have been reported in experiments involving metal samples irradiated with ions in several energy ranges [2–6]. These patterns strongly remind the phenomenology of liquid films dewetting from their substrate. Under this suggestion, it has been proposed that also ion-irradiated metal films can dewet from their substrates following mechanisms that can be assimilated to those of the liquid phase. As much study has been devoted to the case of liquids films [7–12], it would be beneficial being able to exploit the knowledge that has been achieved also in the case of ion bombardment. The understanding of the underlying mechanisms is crucial for many applications, ranging from coatings and their stability in harsh environments, to nanofabrication techniques exploiting self-organization processes. In this paper, we explore in detail the applicability of the liquid model to experiments of ion irradiation, with a focus on the prediction of its numerical implementation, and, in particular, the effect of substrate topography on the morphology of the film after irradiation. The final aim is to provide a simulation tool able to guide experiments and production processes.

2. Materials and methods

Degreased p-doped (100) silicon (Siltronix Sas, Site d'Archamps, France), covered with its native oxide layer, was used as substrate for polystyrene and chromium films. Since in the case of liquid dewetting, the purpose was only to explore the phenomenology of the possible morphologies, polystyrene (diluted in toluene) was deposited from a drop. Because of the shape of the sessile drop, this choice allowed for the observation of regions with different thicknesses in one single sample. Optical images were acquired with an upright microscope equipped with a CCD camera (microscope BX51, camera F-View II, Olympus Co. Ltd, Shinjuku, Tokyo, Japan). On the contrary, a uniform thickness was obtained for chromium films that were deposited in a turbo pumped magnetron sputtering system (Emitech K575X, Emitech Ltd., Ashford,

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Kent, UK) equipped with a quartz crystal microbalance. 30 keV Ga^+ ion irradiation and concurrent imaging were performed in a focused ion beam-scanning electron microscopy (FIB-SEM) system (CrossBeam 1540xb, Carl Zeiss AG, Oberkochen, Germany). In all cases but that of the finger instabilities, a defocused rastering ion beam was used. The 800 nm spot size compared to a typical ~10 nm pixel size deriving from the magnification chosen in the experiments, guarantees that no effect can be ascribed to the rastering process. Ion currents between 5 and 50 pA and a dwell-time of 12 μs, allowed for the selection of fluences ranging from 4×10^{14} ions/cm^2 to 4×10^{15} ions/cm^2 per frame.

3. Theory, results and discussion

In the top line of Fig. 1, optical microscopy images exhibit the most typical patterns usually encountered in experiments involving liquids. Panel (a) refers to the central part of the drop. In this region, where the drop is expected to be thicker, we could observe the nucleation of holes, while moving towards the rim, where the film is thinner, optical imaging shows the typical percolated pattern of spinodal dewetting (Fig. 1b). On the rim, where the contact line is receding, typical finger instabilities can be observed (Fig. 1c). Bottom line of Fig. 1 shows experiments with similar output involving Ga-irradiated Cr films. The strong similarity of these patterns was a motivation to deepen the analogies between the two systems. In the following, we start with a short description of the theory of liquid dewetting, introducing concepts that will be readily applied to the case of ion irradiation. For this class of experiments, we discuss the implementation through a numerical model, and we go through some predictions and experimental verifications for this model.

3.1. Dewetting of liquids

The stability of a liquid on a solid surface is usually analyzed by considering the profile of the liquid-vacuum or vapor (LV) interface that minimizes the system free energy. With reference to Fig. 2(a), if $v(x, y)$ represents the topography of the substrate, and $u(x, y)$ the profile of the LV interface, the system free energy will be a functional $F[u, v]$ that can be obtained by integrating the energy density:

$$f(x, y) = \begin{cases} \gamma_{SV} & \text{dry} \\ \gamma_{SL} + \gamma\sqrt{1 + (\nabla u)^2} + \Phi(u - v) & \text{wet.} \end{cases} \quad (1)$$

Here γ_{SV}, γ_{SL}, and γ are, respectively the solid–vacuum (SV), solid–liquid (SL), and LV interfacial tensions (surface tension). The potential $\Phi(h)$, which is function of the distance h between the LV an LS interfaces, is due to long range interactions, and effectively expresses an attraction or a repulsion between the film and the substrate. When the distance is larger than the molecular size h_c, $\Phi(h)$ is controlled by Van der Waals (VdW) forces, i.e. $\Phi(h) = A/12\pi h^2$, where A is an effective Hamaker constant accounting for the energetic properties of the different materials involved [11–13]:

$$A = \left(\sqrt{A_S} - \sqrt{A_L}\right)\left(\sqrt{A_L} - \sqrt{A_V}\right). \quad (2)$$

For $h < h_c$, repulsive forces become active, and different expressions can be found for Φ in this region [11,14]. However, consistency between the two terms in Eq. (1) requires $\Phi(h \to 0) = \mathcal{S} = \gamma_{SV} - \gamma_{SL} - \gamma$ [15]. Under these assumptions, for a slowly varying profile of the LV interface, it is easy to show that the optimum profile will minimize the functional

$$F[u, v] = \int_{\text{wet}} \left[-\mathcal{S} + \frac{1}{2}\gamma(\nabla u)^2 + \Phi(u - v)\right] dS. \quad (3)$$

A linear stability analysis of Eq. (3) shows that a liquid film is unstable when $\Phi'' = d^2\Phi/d^2h < 0$: for a VdW potential this means that to observe dewetting a $A < 0$ is required. For example, this occurs usually for a metal film on a non-metal substrate, but not for the reversed combination. In case of instability, all the Fourier components with a wavelength longer than the cut off $\lambda_c = \sqrt{4\pi^2\gamma/\Phi''}$ will be exponentially amplified with a fastest growing wavelength $\lambda = \sqrt{2}\lambda_c$ that first will break the film and characterize the final morphology. The time constant for the exponential growth of the fastest growing wavelength is

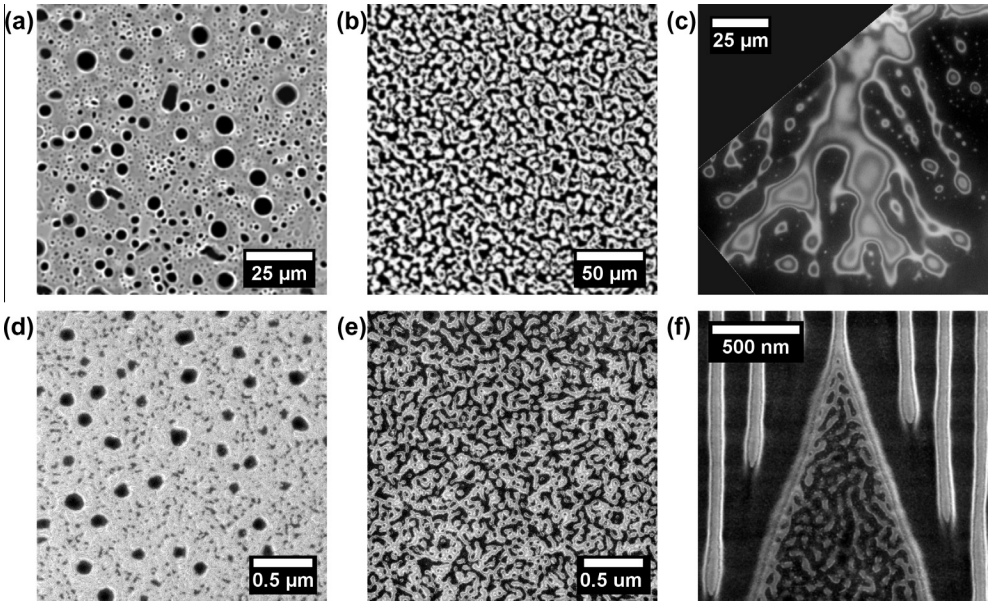

Fig. 1. Phenomenology of dewetting for liquid films and ion-irradiated solid films. (a–c) Optical microscopy images of a polystyrene film dewetting from silicon: (a) heterogeneous nucleation, (b) spinodal dewetting, (c) finger instabilities. (d–f) SEM micrographs of Cr films deposited on silicon under 30 keV Ga^+ irradiation. (d) Nucleation, (e) spinodal-like pattern, (f) finger-like structures. (Non-linear look-up table have been applied to optical images to point out the similarities with the SEM analogues.)