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Grain growth: The key to understand solid-state dewetting of silver thin films

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ABSTRACT

The dynamics of solid-state dewetting of polycrystalline silver thin films in oxygen atmosphere was investigated with *in situ* and real-time environmental Scanning Electron Microscopy at high temperature combined with Atomic Force Microscopy. Three steps were identified during dewetting: induction, hole propagation without specific rim and sintering. Moreover, it was observed that a very selective grain growth, promoted by surface diffusion, plays a key role all along the process.

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Continuous polycrystalline metallic films are metastable when deposited on a substrate they do not wet [1]. Their spontaneous evolution with time or upon appropriate annealing results in very specific nanostructures or patterns with high potential of applications in optics [2] and optoelectronics [3]. This process is called dewetting, because the initial continuous layer breaks up into particles [4] as would a water film do on a hydrophobic surface. This transformation is governed by the decrease of the total interfacial energy of the system [4,5]. Yet in the case of solid-state dewetting, it happens through diffusive mass transport along the surface, the interface or grain boundaries [4,6,7]. Moreover, as solid crystalline surfaces exhibit inherent anisotropy, the knowledge of diffusion paths is crucial to understand the dewetting kinetics [8] and the resulting morphology of the dewetting layer [9].

So far, dewetting was commonly described to occur in two steps. First, during an induction or incubation period, hillocks appear although the substrate coverage by the film is apparently not modified [4]. Hillock growth is often assumed to result from the compressive stress arising from differential thermal expansion upon annealing [4]. In the second step, holes appear within the film and grow [4,5,10]. Hole expansion is due to curvature differences between the dewetting front and a propagating rim [1,11]. Indeed, according to Fick's first law, the driving forces for diffusion are local fluctuations in chemical potential which is directly linked to surface curvature [11]. Finally, the rim is transformed into isolated islands due to Rayleigh instabilities [1]. However, the exact morphology of both dewetting front and propagating rim have been long-discussed. In the first capillary models, the rim was round shaped [11,12] and the layer behind it was depleted [11]. Later, Jiran and Thompson [8], suggested that the front was as thick as the layer without any rim. Surface energy anisotropy was considered later on, but on a rim observed in dewetting on single-crystals [13,14]. Based on *ex situ* observations, they adapted capillary approach to single-crystal case by including solid diffusion.

More recently, the role of grains in dewetting of polycrystalline layers started to be discussed in the literature [10,15,16,17]. In this regard, new insight on the role of grains and dewetting in general was brought by *in situ* techniques, naturally allowing for more accurate kinetic data compared to interrupted annealing [18] Kosinova et al. [6,9] studied hole propagation by *in situ* Atomic Force Microscopy (AFM). They observed grain growth at the edge of the hole and behind the first grain row. A new model was suggested, where hole propagation was due to successive growth and shrinkage of neighboring grains coupled by interface diffusion. This diffusion was found to depend on the surrounding atmosphere [6,9]. Atiya et al. [16,17] showed that the dewetting of platinum thin films supported on $SrTiO_3$(100) is clearly impacted by the orientation of the substrate. They observed that grains having specific crystallographic orientations play an important role in hole propagation morphology and kinetics.

However, real-time imaging of the kinetics of dewetting is still lacking to really unravel the evolution and actual existence of a dewetting

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rim and the role of grains in the process. The present work is dealing with the dewetting morphology of a polycrystalline silver thin film as observed by *in situ* real-time Environmental Scanning Electron Microscopy (ESEM) and AFM. Amorphous silica was selected as a substrate to get rid of epitaxy issues and its poor surface energy anisotropy [19] makes silver a good candidate for capillary approach. Moreover, its sizable surface diffusion in oxygen [20] allows experiments to be run at moderate temperatures. Our results show that dewetting proceeds in three steps: induction, hole propagation and sintering, which are driven to a large extent by the extraordinary growth of specific grains.

All studied films of 20 or 40 nm (±1 nm) thicknesses were deposited at room temperature by pulsed current magnetron sputtering (power: 210 W; deposition rate: 1.3 nm/s; Ar pressure: 8.10^{-3} mbar) on silicon wafers covered with their native oxide. Thicknesses were determined by AFM step measurement and the initial film roughnesses (measured by AFM) were in the range of 5.0 nm (Root Mean Square). SEM experiments were performed with a FEI Quanta 200 ESEM FEG apparatus in a 400 Pa oxygen atmosphere. A dedicated *in situ* heating stage allowed controlling very accurately the sample temperature (25–400°C) through a thermocouple placed close to the sample [21]. The heating ramp (50 °C/s) was fast enough to reach the setpoint temperature (±5 °C) before the apparent onset of hole propagation. Two magnifications were used: ×3000 to have statistical data for morphology and coverage analysis and ×20000 to investigate the dewetting mechanism and grain growth at smaller scale. The fast video rate (20 images/min) allowed following the dynamics of the dewetting front. A careful image processing was performed with Sckikit-image library in Python. After a (2,2) median filtering, the segmentation parameter was chosen for each image as the lowest minimum between the two highest maxima of the gray level histogram. To ensure that measured values were statistically satisfying, test were done on cropped images. The measured intensity values remained unchanged (less than 2% difference), excluding any size effect. A Bruker Dimension Icon AFM equipped with a heating stage was used in tapping mode to image topography during dewetting in air. The sample was annealed (below 150 °C) for an appropriate time (as indicated below) and cooled down to ambient temperature to image topography.

Continuous SEM videos at different temperatures were recorded, from the continuous thin film state to the final particle state (Fig. 1; see supplementary material online; Video 1 at ×3000 magnification and 390 °C and Video 2 at ×20000 magnification and 330 °C). The real-time monitoring shows distinctly that dewetting proceeds in three steps: (i) a period of induction/incubation where the covered surface hardly evolves [4], (ii) a hole propagation with a complex evolution of the dewetting front *i.e.* the limit between covered and uncovered surface, and (iii) a long-lasting late evolution of isolated worm-like particles which become more regular and agglomerated. Although thermodynamics predicts the formation of round shaped particles, they are not observed even after 30 min annealing (see Video 2) suggesting that the dewetting is still not over. In the first studies [8], it was assumed that final particles were formed directly after the isolation of metal domains. Yet a more recent Tranmission Electron Microscopy work highlighted a film evolution after hole impingement [15], coherent with our observations. Extraordinary grain growth is another dominant feature of hole propagation in our present study on polycrystalline silver layers on amorphous substrate. It occurs close to the holes but also far away, as observed in iron/sapphire system [7]. For instance, in Fig. 1, the distance from the dewetting front (blue line) to a growing grain isolated on the continuous film (green line) is about 1 μm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To rationalize these observations, images were analyzed to extract the ratio of covered surface, the front length and the number of holes from Video 1 (Fig. 2). Although the limit between induction and hole propagation is quite clear [4] *i.e.* the onset of the variation of substrate coverage (marked by a full line in Fig. 2), the transition to sintering

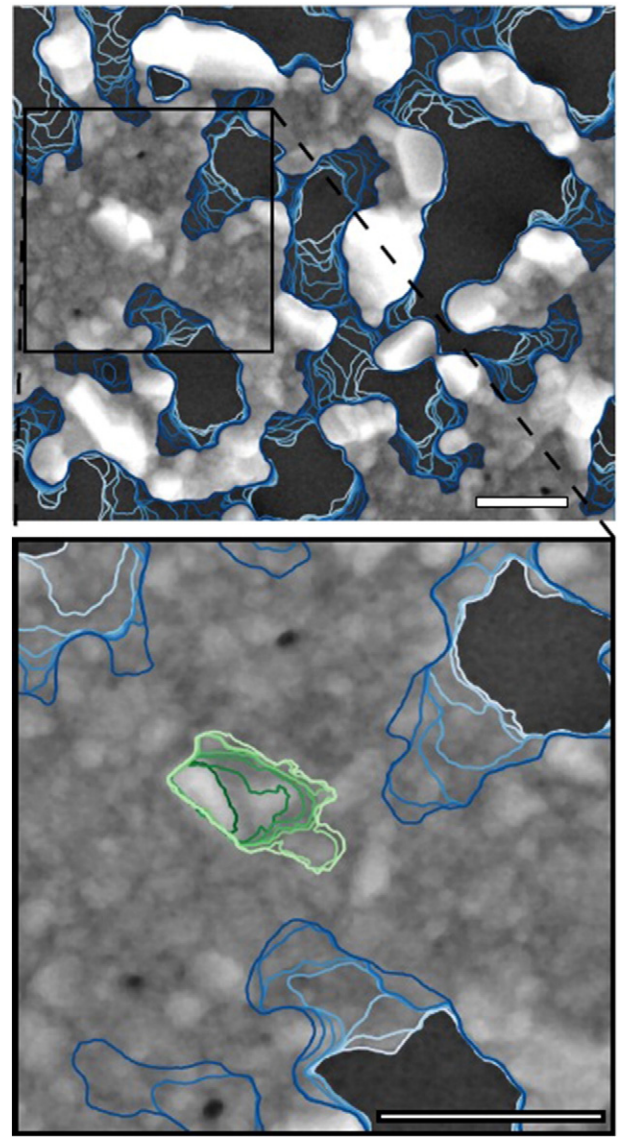

Fig. 1. *In situ* SEM observation of solid-state dewetting on a 40 nm thick silver film on silica held at 330 °C under 400 Pa O_2. Blue lines represent the time evolution of the front propagation, the lighter being the older. Green lines represent the grain boundary, the darker being the older. The scale bar is 1 μm.

calls for a peculiar analysis. In Fig. 2, three events happen simultaneously (marked by a dashed line in Fig. 2) (i) the abrupt change of substrate uncovering rate, (ii) the maximum in front length, (iii) the impingement of holes into a percolated or interconnected domain. This specific time represents the limit when the entire initial layer has been modified by dewetting and when only agglomerated and isolated particles remain. When holes propagate, the front length increases, but on the contrary, it decreases when agglomerated particles sinter. In this state, besides slow Ostwald sintering, intra-particle mass transport is required to change the substrate coverage. This explains the variation of the uncovering rate, even with the same diffusion mechanisms. For these reasons, we suggest to define this time point as the global limit between hole propagation and sintering.

As already highlighted, all along the three-step process of dewetting on those polycrystalline layers, grain growth plays a key role. On Video 2 of supplementary information, the image sequence begins shortly before the hole propagation step, at the end of induction time. At this point, grown grains are already observed (see Fig. 3a). Since SEM

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