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# On the solid-state dewetting of polycrystalline thin films: Capillary versus grain growth approach

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ABSTRACT

Solid-state dewetting of polycrystalline silver thin films was investigated with *in situ* and real time Environmental Scanning Electron Microscopy at High Temperature (HT-ESEM) in different annealing atmospheres: secondary vacuum or oxygen-rich (partial pressure $\geq$100 Pa) environment. A model where oxygen plays a key role is proposed to explain the very different observed morphologies; oxygen favours hole creation and isotropic hole propagation as well as grain selection. But, whatever the atmosphere, dewetting does not proceed through the propagation of a rim but instead involves the growth of specific grains and shrinkage of others. Models based on macroscopic curvature to account for the propagation speed of the dewetting front fail to fit the present observations. This points to a paramount role of the grain size and stability in the dewetting morphology.



## 1. Introduction

During the last few years, an increasing research effort has been dedicated to the solid-state dewetting of metallic thin films [1,2]. It is identified as a potential way to produce at will metallic structures for numerous applications among which photovoltaic systems or sensors [3] or for low-cost templated fabrication processes at the nanoscale [4]. However, for each application, the control of the morphology obtained through dewetting is crucial. In this respect, the understanding of the physical phenomena driving dewetting in polycristalline films has been greatly improved. The role of grains has been underlined [5–7], new diffusion pathways have been identified [8,9] and the role of crystalline orientation in anisotropic materials has been explored [10]. New approaches have been employed and developed to monitor dewetting morphology *in situ* (Atomic Force Microscopy, AFM [9]) and in real time (Scanning Electron Microscopy, SEM [5], Spectroscopic Ellipsometry, SE [11], Transmission Electron Microscopy, TEM [12,13]). These techniques have brought valuable information about the importance of grains in the kinetics of dewetting and the evolution of metallic structures and of holes.

Nevertheless, a consensus in the description of solid-state dewetting has not been reached. Historically, the first model was based on capillary approaches, inspired by liquid dewetting [14], which neglect the crystalline nature of the film. The surfaces are considered as homogeneous and isotropic; the local curvature and the associated gradient of chemical potential is suggested to be the driving force of the material transport. The model implies the propagation of a rim at the dewetting front [14]. However, Jiran and Thompson [15] observed that the rim was not homogeneous, and that the dewetting rate was strongly dependent on its size. The smaller the rim, the faster the propagation. In order to address the specificity of solid surfaces (*i.e.* anisotropy and faceting), the concept of mean-curvature [10] was introduced in the models. Of particular relevance for single crystals [10,16], it was also used for polycrystalline films [7,17]. However, in the latter case, the grains are shown to play a non-negligible role [5,7] leading to a very different approach in which the phenomena involved in the dewetting are related to grain assembly evolution. For instance, the propagation of a rim becomes the successive growth and shrinkage of grains [18]. Instead of a continuous surface, grains are considered

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as discrete entities exchanging material through specific surface or interface mass transport [9]. Here, the chemical potential is directly linked to the size of the grain.

Yet the diversity of studied systems is a great source of complexity in this field of research [1,2]. From crystalline to amorphous substrates, from films in epitaxy on single-crystals to polycrystalline deposit, dewetting can exhibit numerous morphologies that strongly depend on the system. In the case of films grown on single crystals, holes can show geometrical and fractal features constrained by surface energy anisotropy. However, shapes are far less regular upon dewetting of polycrystalline films, in particular on amorphous substrates. In this regard, it is difficult to set up a unique model that applies to any system. For instance, by comparing the dewetting of two different polycrystalline metallic layers, copper and gold [19], Kvon et al. have suggested that two very different mechanisms are responsible for the hole creation within the films. They assign this to the relative difference between the metal surface energy and the grain boundary (GB) energy. In the case of gold, a morphology of type "nucleation and growth" is observed and was explained with a Diffusion Limited Aggregation model (DLA) while the concomitant appearance of many holes in the Cu film is attributed to the grooving of grain boundaries.

In the case of silver layers, such different morphologies were already observed but in different works. Simrick et al. [20] studied the thermal stability of silver layers (100–820 nm) evaporated on a single-crystal of ytrria-stabilised zirconia (YSZ). They ascribed the hole propagation to the grooving of surrounding grains. The morphology they observed is similar to that of the copper observed by Kwon et al. [19]. At the opposite, Roy et al. [21] observed a fractal morphology of silver depleted regions (probably that we refer as "holes"). The silver layer (125 nm) was deposited by thermal evaporation on a Br-passivated Si substrate, preventing the formation of silicium oxide. They also described holes propagation in terms of GB grooving, and suggested that the fractal shape of the holes was due to the initial structure of the GB. This latter morphology is similar to that of gold observed by Kwon et al.

To our knowledge, no work draws a direct comparison of the two different morphologies for the same layer on the same substrate. In the present work, the question of variability of the dewetting morphology is tackled by considering the same system in different annealing atmospheres, namely polycristalline silver on amorphous silica. This substrate has been chosen to prevent the behaviour of the film from being dictated by preferential crystalline orientation on the substrate. Dewetting was studied thanks to *in situ* and real time SEM [5], in different annealing atmospheres, *i.e.*, in the secondary vacuum of the SEM chamber or under near ambient pressure of oxygen (typically 100–400 Pa). The very different observed morphologies are tentatively explained by a simple model and the role of local curvature in the speed of the propagation front is examined through accurate image analysis.

## 2. Experimental and image analysis

Silver films were deposited by magnetron sputtering (Ar pressure: $8.10^{-3}$ mbar, power: 0.35 W/cm$^{-2}$, rate: 1.3 nm/s, target/sample distance: 8 cm) onto polished (100) silicon wafers covered by their native oxides. Wafers were used as received without specific treatment. The thickness of the film (from 15 to 80 nm) was controlled by AFM on a step created on purpose in the layer. *Post mortem* AFM pictures were acquired on a AFM Dimension Icon microscope (Bruker). All data were recorded at room temperature after the sample had cooled down. SEM experiments were performed with a FEI Quanta 200 Environmental SEM FEG (Field Effect Gun) apparatus in a controlled atmosphere. A dedicated *in situ* heating stage allowed controlling very accurately the sample temperature (between 25 and 600 °C) through a thermocouple placed in direct contact with to the sample [22]. The residual pressure in the chamber was about $10^{-3}$ Pa and it will be referred to as "vacuum" condition hereafter. High purity oxygen could also be introduced in the chamber up to a partial pressure of 400 Pa. This environment will be referred to as "oxygen". Images were recorded either at high magnification (typically × 10000) to study local details of the dewetting layer and to determine the local curvature, or at low magnification ( × 3000) to analyse statistical evolution. When compared, image sequences were recorded from parts of the same initial silicon wafer, ensuring the layer was rigorously the same. Dewetting in vacuum was also studied by TEM on films deposited onto electron transparent amorphous silicon nitride grids. A Tecnai F20 apparatus was run in imaging mode at 200 keV, coupled with Automatic Crystal Orientation Mapping (ACOM). ACOM consists in an analysis, pixel by pixel, of the electron diffraction pattern. The local crystalline orientation is reconstructed by fitting the obtained patterned with that calculated from a tilted model crystal. The pixel size ($\approx$5 nm) is larger than that of the probe footprint, which is identical to the TEM in imaging mode, < 1 nm. Data analysis was performed with the Astar-package [23]. Due to acquisition time and stability constraints of mapping, experiments were performed at room temperature, after annealing, also preventing further dewetting and change during acquisition. Moreover, the electron beam was directed off the analysed zone during annealing to prevent it from perturbing the dewetting process. Despite the use of different amorphous substrates and imaging techniques, very similar morphologies were found between SEM and TEM runs, further confirming the robustness of the findings.

Specific image processing strategies were developed by using Scikit-Image and Numpy libraries in Python. The local curvature of the dewetting front and its speed of propagation were extracted from the SEM image sequences as follows. First, a segmentation as described in a previous paper [5] is applied to two consecutive images $n$ and $n+1$. The contours of the segregated regions are then extracted with the built-in function *skimage. measure.find_contours* and fitted with a Spline method (function *scipy. interpolate*), allowing to calculate easily the local in-plane curvature $\kappa_{\parallel}$ at each interpolated point. The resulting normal vector at each position of the front in image $n$ is then propagated until it reaches the contour of the image $n+1$. The obtained distance divided by the delay of acquisition gives the local speed $s$ of the front at a given point of curvature $\kappa_{\parallel}$. This gives rise to a histogram of occurrence $n(\kappa_{\parallel}, s)$. However, some curvatures are far more frequently observed than others, and the results should be normalized for the sake of consistency. To understand this, let's consider a circle growing at a constant rate. Obviously, the number of points necessary to describe it grows linearly with its radius. In the corresponding raw $n(\kappa_{\parallel}, s)$ histogram, the points at higher curvature (smaller radius) appear less dense than the others. But the physical observation is that the speed of growth is independent from the curvature. To account for that, it is necessary to normalize by the probability of occurrence of a given curvature $n(\kappa_{\parallel})$ and to consider the conditional probability $P(s|\kappa_{\parallel})$ to observe a given speed knowing the curvature:

$$P\left(s\middle|\kappa_{\parallel}\right) = n\left(\kappa_{\parallel}, s\right) \Big/ n\left(\kappa_{\parallel}\right). \tag{1}$$

To better interpret the following experimental histograms of $P(s|\kappa_{\parallel})$, let's consider pedagogical examples as illustrated in Fig. 1. A linear front has a curvature constant and equal to zero. If it propagates at a speed $s = V_0$, then $P(s|\kappa_{\parallel})$ consists in a unique point at coordinates $(\kappa_{\parallel} = 0, s = V_0)$. A circular hole of radius $r$ expanding at constant speed $s = V_0$ has a curvature $\kappa_{\parallel} = -1/r$ (this curvature