The role of abnormal grain growth on solid-state dewetting kinetics

Galit Atiya,[a] Dominique Chatain,[b] Vissarion Mikhelashvili,[c] Gadi Eisenstein[c] and Wayne D. Kaplan[a,*]

[a]Department of Materials Science and Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel
[b]Aix Marseille Université, CNRS, CINaM UMR 7325, Marseille, France
[c]Department of Electrical Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel

Abstract—Continuous thin films of Pt on A-plane $(11\bar{2}0)$ sapphire substrates were dewetted to characterize the morphological evolution and dewetting kinetics at 800 °C using an oxygen partial pressure of 10^{-20} atm. Hole growth was studied, focusing on partially dewetted samples. Four different low-index orientation relationships were found between the Pt and sapphire substrate by electron backscattered diffraction combined with transmission electron diffraction patterns. Abnormal grains adjacent to the holes with a small deviation from one of the low-index orientation relationships were observed. The difference in the heights of the abnormal grains adjacent to the holes (rim-height) is influenced by the initial position of the hole, and the existence of grains with a low-energy interface orientation relationship, and not only by diffusivity rates dictated by surface orientation as described in existing edge-retraction models. The existence of low-index orientation relationships is seen as the driving force for abnormal grain growth in the vicinity of the holes, and is a dominant factor in controlling the dewetting rate of thin metal films on oxide surfaces.
© 2014 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Interfaces; Abnormal grain growth; Crystallographic orientation; EBSD; Solid-state dewetting

1. Introduction

The mechanism(s) and kinetics of dewetting of thin films have been extensively investigated over the last few decades, in an attempt to understand the dominant mechanism which controls the dewetting process. It is well known that thin films are not stable and tend to break up into isolated particles (or droplets in the liquid state), where the dewetting process is driven by minimization of the total surface/interface/grain boundary energy. Dewetting is commonly used for microelectronic applications to form nanometer length-scale crystals for silicon-on-insulator structures [1,2], catalysts for growth of carbon nanofibers and nanotubes [3], and electrical memory and optical devices [4,5].

Without a detailed understanding of the mechanisms and kinetics of the dewetting process, its technological application to form specific structures and arrays will be limited. Different parameters affect the dewetting kinetics and the final particle morphology, such as the initial film thickness, the film deposition method, alloying elements, the temperature used for dewetting, and the partial pressure of gas species (in particular oxygen) [6–11]. While solid-state dewetting depends on many parameters, it can be divided into three main stages: hole nucleation and grain growth (for polycrystalline thin films), hole growth and "finger" formation, and film break-up. The first stage (hole nucleation) was originally modeled by Mullins who showed

that for polycrystalline films grain boundaries and grain boundary triple junctions play an important role in the nucleation of holes [12,13]. Assuming that grain boundary grooving is the initial mechanism for hole nucleation, Srolovitz and Safran used the ratio of surface to grain boundary energy to establish criteria for hole nucleation [14]. Based on initial results indicating that void nucleation at metal-oxide interfaces may lead to the nucleation of holes [15], Shaffir et al. conducted controlled solid-state dewetting experiments of gold on zirconia, which showed that hole nucleation can initiate at relatively high energy metal-oxide interfaces via nucleation of voids [16]. Hole nucleation (via grain boundary grooves or void growth from the interface) may occur concurrently with grain growth of the initially continuous polycrystalline thin film. Grain growth is driven by reduction of the total grain boundary area to minimize grain boundary energy [17]:

$$\frac{d\bar{r}}{dt} = \bar{m}\bar{g}_{gb}\bar{k}, \tag{1}$$

where $\bar{r}$ is the average grain radius, $\bar{\gamma}_{gb}$ is the average grain boundary energy, $\bar{m}$ is the average grain boundary mobility, and $\bar{k}$ is the average boundary curvature. The influence of grain growth on hole nucleation has been the focus of several theoretical studies, indicating that at a stagnated grain size (radius) of $R_{Stagnation} \approx \gamma_f^h / \gamma_{gb} \approx 2.5h$, where h is the film thickness, the driving force for further growth of normal grains decreases significantly and the preferential growth of grains with specific crystallographic orientations will be favored [18,19].

Abnormal grain growth (AGG) in thin films was simulated by Frost et al. to estimate the driving force for AGG without the influence of holes [20]. Simulations showed that only minor changes in the free surface energy between adjacent grains is required to drive AGG. Abnormal grains were seen by Müller and Spolenak at the edge of holes during dewetting of Au films on $SiN_x/SiO_2/Si$ [21].

The second step in dewetting is hole growth, which occurs via film edge retraction. The first model for the edge-retraction phenomena was based on experimental observations and was proposed by Brandon and Bradshaw [22]. In their model, assuming single-crystal films and isotropic surface energies, surface diffusion resulted in mass accumulation and the formation of a rim at the edge of the hole. When the rim becomes larger the hole growth rate decreases due to the decreasing radius of curvature [22]. Jiran and Thompson, using the model from Srolovitz and Safran, modified the Brandon and Bradshaw model, explaining that a perturbation in the rim around the hole allows for surface diffusion in all directions, and break-up into fingers and then islands (the so called "fingering instability"), thus facilitating the dewetting process [23,24]. The evolution of the shape and position of the retracting rim was also addressed via different models [24–27]. Srolovitz and Safran assumed isotropic surface energies, and noted that the depth of the valley which forms after the rim increases as the edge retracts, until it contacts the substrate which leads to pinch-off [24]. Klinger et al. described the retraction kinetics of single-crystal films of a fully faceted edge with highly anisotropic surface energies, and concluded that the formation of hills with the absence of a depression indicated "strong anisotropy" of the edge and results in slow-down of dewetting [25]. More recently, Zucker et al. demonstrated that the retraction distance of a faceted edge as a function of time corresponds to $x_0 \propto t^n$ (where $n = 0.436$), and that the rim height and width depend on $n = 0.254$ and $n = 0.193$, respectively [26]. The two first kinetic models described above assumed isotropic surface energies and the absence of grain boundaries, which is clearly not the case for polycrystalline films. While Zucker et al. took anisotropic surface energies into account, the influence of grain growth on the kinetics of dewetting was not considered, although it may have a significant effect on the dewetting mechanisms which control the dewetting rate.

Dewetting experiments are also often used to extract kinetic parameters such as the surface diffusion coefficient [28,29]. This form of analysis was first used by Jiran and Thompson via the correlation of film coverage as a function of time [30]:

$$X_{dewet} = 1 - \exp\left[-N_h \pi v_h^2 (t - t_i)^2\right], \tag{2}$$

where X_{dewet} is hole coverage area, N_h the number of holes, t_i is the incubation time, $v_h = \frac{2D_s v_s \Omega^2 \gamma_{fv}}{kTh^3}$ where D_s is the coefficient for surface diffusion, Ω is the atomic volume, v_s is the number of surface atoms, γ_{fv} is the surface energy, k is Boltzmann's constant, T is temperature and h is the film thickness.

However, the dewetting kinetics may be influenced by additional microstructural parameters, such as surface/interface perturbations, interface energy, grain boundary energy, etc. As will be demonstrated here, hole formation and growth in thin films is often heterogeneous, and the coverage as a function of time varies with the position of the hole across the substrate. In addition, the approach summarized in Eq. (2) assumes a constant rate of growth of dewetted areas and a constant number of hole nuclei, and ignores microstructural aspects of the dewetting process, including hillock formation, interface void nucleation and the influence of triple lines intersecting the substrate on hole nucleation and growth. The current study focuses on the phenomenon of AGG adjacent to holes during solid-state dewetting, and how AGG may influence the kinetics of dewetting. In addition, the influence of low-index orientation relationships (ORs) between the film material and substrate on the hole growth rate and AGG is addressed.

2. Experimental methods

2.1. Sample preparation

Sapphire substrates (99.99% purity) with $(11\bar{2}0)$ parallel to the substrate surface (A-plane orientation) were provided by Gavish Industrial Technologies & Materials (Omer, Israel). Polished substrates were ultrasonically cleaned in acetone and ethanol, and thermally annealed for 2 h at 1100 °C in Ar + 2%O_2. 50 nm thick Pt films were deposited by electron beam evaporation at ambient temperature, at a deposition rate of $\sim$0.1–0.2 Å s^{-1} under high-vacuum conditions (2×10^{-7} Torr). Annealing at 800 °C for different periods of time was conducted to (partially) dewet the films, using a heating and cooling rate of 10 °C min^{-1}. The shortest annealing time (1 min) was conducted to examine the influence of heating and cooling rates. Dewetting was conducted in a sapphire tube furnace under flowing Ar + H_2 (99.999%) at a partial pressure of oxygen $P(O_2) < 10^{-20}$ atm.

2.2. Characterization methods

The bare (α-Al_2O_3) surface morphology after annealing in Ar + O_2 at 1100 °C for 2 h was characterized using atomic force microscopy (AFM; Omnicron-UHV-SPM). The as-deposited microstructure was characterized by X-ray diffraction (XRD; Rikagu Smart Lab X-ray Diffractometer at $\lambda = 0.1540598$ nm) and the film thickness was confirmed by cross-section microscopy on samples prepared using a dual-beam focused ion beam system (FIB; FEI Strata 400 s).

The dewetted film morphology was characterized by high-resolution scanning electron microscopy (HRSEM; Zeiss Ultra-Plus FEG-SEM) after coating the samples with a thin carbon layer to avoid charging under the electron beam. An FEI E-SEM Quanta 200 scanning electron microscope equipped for electron backscattered diffraction (EBSD) was used to determine the misorientation between Pt grains, and the OR between Pt grains and the sapphire substrate (using HKL software).

The grain size distribution and film coverage as a function of dewetting time was analyzed from HRSEM micrographs. To determine the grain size, a Matlab program was used for $\sim$300 grains for each sample [31]. The coverage was analyzed using Image J [32]. The volume of Pt diffused from the hole to the hole-rims was determined from contact-mode AFM data [33].

High-resolution transmission electron microscopy (HRTEM) was conducted using a monochromated and (image) aberration corrected microscope (FEI Titan 80–300 kV S/TEM). Site-specific TEM sample preparation was conducted using the in situ lift-out technique [34,35].