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Crystallographic analysis of the solid-state dewetting of polycrystalline gold film using automated indexing in a transmission electron microscope

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We analyzed the effect of crystallographic anisotropy on the morphological evolution of a 12-nm-thick gold film during solid-state dewetting at high temperatures using automated indexing tool in a transmission electron microscopy. Dewetting initiated at grain-boundary triple junctions adjacent to large grains resulting from abnormal grain growth driven by (111) texture development. Voids at the junctions developed shapes with faceted edges bounded by low-index crystal planes. The kinetic mobility of the edges varied with the crystal orientation normal to the edges, with a predominance of specific edges with the slowest retraction rates as the annealing time was increased. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4937432]

Thin films on solid surfaces are energetically metastable because of their high surface-area-to-volume ratio, and they will dewet or disintegrate into agglomerates at high temperatures. The dewetting can be guided or controlled at the nanoscale by using templates with topography, pre-pattern the films, or employing an irradiating interfering laser beam;1–3 this nanoscale control may provide a path to incorporating dewetted films in applications such as patterned magnetic recording media,4,5 plasmon resonance waveguides,6,7 plasmon-enhanced photovoltaic devices,8–11 and catalysts for nanowire growth.12

In polycrystalline metallic films, solid-state dewetting (SSD), which occurs below the melting point, starts with hole formation at a grain-boundary triple junction, proceeds with the retraction of the void edges by capillary-driven diffusion, and is completed with the formation of particles due to a Rayleigh-like instability of ligaments.13,14 This phenomenology has been treated in various analytical models.15–17 However, because of anisotropy in the surface energy and diffusion coefficients at different edges, the dewetting process is affected by the crystallographic orientation of the original film. This has been mostly explored using single-crystal films, where the surface-energy anisotropy typically results in faceted void edges and affects the edge retraction rate or direction and further pinch-off behavior. For example, for (001)-oriented Si films on silica annealed at 800 °C, facets that are rectangularly bounded by edges parallel to the {110} crystal planes form initially; then, the hole corners rapidly retract and branch to develop star-like-shaped holes.18–20 Ye and Thompson21 measured the edge retraction rate as a function of the initial in-plane orientation of the edge using pre-patterned single-crystal Ni films, and presented the results as “a kinetic Wulff plot” that exhibited sharp minima of the retraction rate at certain in-plane orientations.

In polycrystalline films, on the other hand, grain boundaries can provide an additional diffusion path, and texture development and grain growth that are concurrent with the dewetting process.
complicate our understanding of the effects of the crystallographic anisotropy. To our knowledge, the lack of research on polycrystalline films is due to the limitations of appropriate analytical methods. In this regard, the analysis of Muller and Spolenak using electron backscattered diffraction (EBSD) in conjunction with scanning electron microscopy (SEM) provided a general understanding of the dewetting evolution in light of crystallographic orientations. However, to precisely determine the effects of crystallographic anisotropy and grain boundaries on initial hole growth and edge retraction, a more detailed analysis using higher-resolution analysis tools is needed.

The present study aims to elucidate the effect of crystallographic anisotropy on morphological evolution during dewetting in thin Au films using an automatic crystal orientation and phase mapping system integrated into a transmission electron microscope. Polycrystalline films on non-reactive substrates or templates have been used to investigate the assembly of ordered nanoparticles via the SSD of thin metal films; thus, we expect that the elucidation of a precise crystallographic phenomenology during SSD in polycrystalline films will provide some technological insight to enable control of both the particle shape and size distribution and to further the texturing of agglomerated particles.

A 12-nm-thick Au film was deposited by RF magnetron sputtering onto a 10-nm-thick silicon nitride support films for TEM (PELCO®). The films were then annealed at 400 °C for 1-120 min in a rapid thermal annealing (RTA) furnace in forming gas (Ar + 4%H2) for ex situ TEM observation of solid-state dewetting. A crystal orientation map was acquired from the TEM samples by beam scanning with a step size of 2.4 nm using an automatic crystal orientation and phase mapping system in TEM (NanoMEGAS ASTAR™). For in situ observation of dewetting process, some as-deposited Au films were annealed in a heating holder for in situ TEM.

Fig. 1 shows the microstructural evolution during heating in in situ TEM. A 12-nm-thick Au film on a silicon nitride support film was heated to 400 °C in the in situ TEM stage at a rate of 50 °C/min with a 10-min hold at each 100 °C increment; an image was recorded at the end of each hold step. As shown in Fig. 1, at temperatures below 300 °C, the grains grew very slowly and no voids were observed. However, when the temperature was increased to 400 °C, the grains grew rapidly and tiny voids formed at the junctions of the grain boundaries. Newly formed voids, as shown in Fig. 1(c), appeared rectangular, but additional images indicated that they exhibited a circular or irregular shape. The void initiation begins after a substantial amount of grain growth has occurred and when the grain boundary movement has subsided. Upon further annealing in the TEM stage at 400 °C, as shown in Figs. 1(d) and 1(e), the holes grew with highly faceted edges, formed nanowires via narrowing ligaments, and finally decomposed into isolated particles.

**FIG. 1.** Grain growth in a 12-nm-thick Au film on a 10-nm-thick silicon nitride film support observed during in situ annealing in the TEM stage. The temperature of the sample holder was increased in 100 °C increments (with an average increase rate of 50 °C/min) and held for 10 min before a subsequent temperature increase. Images were recorded at the end of the hold time for (a)–(c), but (d) and (e) were acquired immediately after and 30 and 60 min after having reached 400 °C, respectively. A and B in the images indicate the same locations.
FIG. 2. Crystal orientation mapping using an automatic crystal orientation and phase mapping system for TEM around holes in a 12-nm-thick Au film after furnace-annealed for 1 min at 400°C under an Ar/4%H$_2$ flow: (a) and (e) crystal orientation map (film normal direction); (b) and (d) correlation index map; (c) BF-TEM image for (d) and (e). The analysis was performed at two different locations in the film ((a) and (b) and (c)–(e)). The maps (b) and (d) emphasize the grain boundaries, and the black lines in (e) denote the grain boundaries with a misorientation $\geq 10^\circ$. The image on the right in (e) is a (111) pole figure analyzed for grain S. If the faceted hole boundary plane, p, is assumed to be parallel to the {111} crystal plane, the line connecting the center to one of the {111} poles in the pole figure for grain S must be normal to the void edge. In this manner, the void edges that are assumed to be parallel to the {111} or {443} crystal planes are denoted by red lines in the holes in (e).

Figs. 2(a) and 2(b) present a crystal orientation mapping image obtained in TEM; this image shows the grains in the Au film around an early tiny hole at the grain boundary. Coarse grains with a {111} out-of-plane texture grew abnormally at the expense of fine grains without other textures, and holes formed at triple junctions adjacent to the large grains. According to previous considerations,23,24 normal grain growth of a film with thickness $h$ stagnates when the grain size reaches $\sim 2.5$ h ($=R_{stag}$), but hole formation occurs at grain boundary grooves$^{25,26}$ and requires grain growth above a critical grain size ($R_c$), which is given by a force balance at the grain boundary junction; thus, for hole formation and growth in the film, $R_{stag}$ should be greater than $R_c$. In this respect, $R_{stag} < R_c$ is assumed for the fine-grain regions in Fig. 2(a), whereas the hole in the figure was formed during subsequent abnormal grain growth driven by the {111} texture development. Further studies of the crystallographic changes during dewetting were carried out using crystal orientation mapping at various stages of the dewetting process. Figs. 2(c)-2(e) show an orientation mapping of the same film shown in Figs. 2(a) and 2(b), but for a region containing a larger number of small holes ($<100$ nm). The overall film developed a {111} out-of-plane texture, as shown in the normal orientation map in (e). The hole edges are curved with straight segments, and some edges extend into the film along high-angle boundaries. There are more voids in regions with greater (111) texture, which supports the theory that abnormal grain growth triggers hole formation.

Changes in the in-plane texture itself may affect hole formation in the film. Assuming that the stress effect is negligible, the free energy change$^{27}$ that drives dewetting can be given by

$$\Delta E_{dew} = (\gamma_i + \gamma_t - \gamma_s) \Delta A_w + \gamma_e \Delta A_e,$$

where $\gamma_s$ and $\gamma_i$ are the surface energies for the substrate and the film parallel to the substrate surface, $\gamma_t$ is the interfacial energy between the substrate and film, and $\gamma_e$ is the surface energy of the film edge at a void. $\Delta A_w$ and $\Delta A_e$ denote the changes in the areas of the film’s top surface and edge surface at a void and have negative and positive values in the dewetting process, respectively.
For dewetting to occur, the following conditions must be met: $\gamma_f + \gamma_i > \gamma_s$ and $\Delta E_{dew} < 0$. In-plane texture development would lower the values of $\gamma_f$ and $\gamma_i$ and thus reduce the driving energy for film dewetting. However, our observations revealed that the holes were mostly formed at large grains with (111) in-plane texture, which implies that the above-mentioned grain size requirement is more important than the effect of the in-plane texture itself. Thermal strain, which is normally compressive, may also affect void formation because it can be relaxed around voids. However, the role of thermal strain is controversial and thus will be dealt in further mechanistic studies with the variation in dewetting temperature.

Fig. 3 presents the crystal orientation map of a film with larger voids, after annealing at 400 °C for 10 min. The film exhibits narrower ligaments but highly faceted voids, and some voids are coalescing. The film was strongly (111) textured. If the faceted void boundaries are assumed to consist of low-index crystal planes, the in-plane projections of the low-index crystal planes of the grain around each faceted hole should be perpendicular to the faceted void edge. Fig. 3(b), for example, shows the pole figures obtained for the A and B grains adjacent to the faceted voids. The void edges at A and B are exactly perpendicular to the in-plane projections of the (111) and (110) planes, respectively. Accordingly, the film boundaries at the hole edges of A and B are assumed to be associated at least with the (111) and (110) crystal planes, respectively. However, the edges perpendicular to the in-plane projection of (111), such as the edge at A, can also be perpendicular to other low-index crystal planes. See supplementary material for detailed information on the crystal planes that bound the void edges. Using this procedure, the crystallographic plane of the faceted edges can be determined and represented by numbers, as illustrated in Fig. 3(b). The (111) plane was prevalent, but other low-index planes were also observed. Most of the faceted hole boundaries

![Figure 3](image-url)
in Fig. 3(a) were indexed, and their frequencies are plotted as a bar chart in Fig. 3(c). Adjacent plane orientations were grouped, as denoted by different colors, and the planes that could not be grouped are presented in gray. The surface energy of each plane relative to that of the (111) plane was obtained from the literature\textsuperscript{33,34} and is also listed in the figure. As shown in Fig. 3(c), the (111) and (443) planes, with the lowest and second-lowest energies per area, are the most prevalent and account for 44.5\% of the total hole boundary length. Using the same procedure, we analyzed the portion of the two lowest energy planes of the total boundary length for the voids in Fig. 2(e) with a shorter annealing time: the hole boundaries with (111) or (443) are denoted as red lines in the holes in Fig. 2(e) and account for 15\% of the total hole boundary length. This result may suggest that the hole boundaries with higher energy retracted faster and gradually disappeared, leaving the lower energy boundaries. The energy consideration in Eq. (1) also supports this conclusion: the surface energy at the film edge becomes prominent as dewetting proceeds, and hence a lower $\gamma_e$, at fixed $\gamma_f$ and $\gamma_i$, increases the driving energy for dewetting.

The plot in Fig. 3(c), however, shows that the faceted hole boundaries still develop a large portion of other crystal planes with somewhat higher surface energies, and a correlation between the surface energy and plane percentage is not evident except for (111) and (443). As shown in Fig. 3(a), some ligaments formed nanowires with a uniform width in which both edge boundaries consisted of the same low-index crystal planes. In Fig. 3(a), the edge boundaries are parallel to the planes (322), (221), or (211), in addition to (111) and (443). This trend indicates that the stability of a hole facet is not simply determined by its surface energy. In Ye and Thompson’s result obtained using a pre-patterned single-crystal Ni film on MgO,\textsuperscript{21} the edge retraction rate exhibited sharp minima at certain initial in-plane orientations of the edge. A two-dimensional edge retraction model for highly anisotropic faceted edges in the same film included other important contributions to the edge retraction rate, such as the surface self-diffusivity on the top facets of the rim, the film thickness, and the film contact angle on the substrate, in addition to the surface energies.\textsuperscript{35} In the present work on Au films on nitride, it is uncertain which factor is the most important for determination of the retraction rate of the hole facets. However, it is clear that the relative frequency of the plane indexes normal to the edges shown in Fig. 3(c) can be regarded as a relative measure of the kinetic stability of the edges against dewetting.

Fig. 4 compares the shapes of the corners of faceted holes. As shown in the top image of the holes in Fig. 4(b), the hole corners at grain boundaries appear sharp, whereas the corners in the grains are blunt. Figs. 4(a) and 4(c) present high-resolution images in which the beam direction is parallel to the [011] crystal orientation of the film. The hole edges are parallel to low-index crystal planes. In Fig. 4(a), the in-plane directions normal to the two faceted edges in the grain are [111] and [111], and the corner of the edges is rounded by monoatomic steps in the $\{111\}$ atomic layers. This rounding can be understood in view of the decrease in chemical potential with increasing curvature of the corner. However, the corner at the grain boundary is not rounded or intrusive along the grain boundary, as shown in Fig. 4(c), in contrast to the intrusive corner of the early tiny voids shown in Figs. 2(c)-2(e). Hence, unlike the early stage of void growth, after the voids form edges with a low-index in-plane normal direction, the grain-boundary diffusion appears to no longer play a significant role in void growth.

![FIG. 4. TEM images of hole corners with and without a grain boundary. The arrows in (a) indicate atomic \{111\} steps at the corner. The circles and rectangles indicate corners with and without a grain boundary, respectively.](image-url)
In summary, we have reported the effects of crystal orientation on the dewetting process of polycrystalline Au films, as determined using an automated crystallographic orientation and indexing tool incorporated into a TEM. Void initiation at the grain boundaries generally requires grain growth above a critical size. In this study, hole formation initiated after abnormal grain growth driven by (111) texture development. The holes initially grew with faceted edges lying along different low-index crystal planes. The retraction rate of the edges varied with the crystal orientation normal to the edges, which resulted in the predominance of edges with specific crystal planes as the annealing time was increased. This observed phenomenology can provide insight into strategies for nanoscale control in the solid-state dewetting processes of metallic thin films with strong texture development and surface energy anisotropy for applications in patterned magnetic recording media, catalysts, and photonic devices.

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32. See supplementary material at http://dx.doi.org/10.1063/1.4937432 for detailed information on the crystal planes that bound the void edges.