Acta Materialia 139 (2017) 51–61

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Solid state dewetting of polycrystalline Mo film on sapphire

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ARTICLE INFO

Article history:
Received 29 March 2017
Received in revised form
14 July 2017
Accepted 29 July 2017
Available online 30 July 2017

Keywords:
Surface diffusion
Theory
Thin films
Grain-growth
Molybdenum

ABSTRACT

We studied the kinetics of solid state dewetting of a thin Mo film deposited on a sapphire substrate. The overall kinetics of the process can be described by the Johnson-Mehl-Avrami-Kolmogorov equation with two different exponents, indicating a decrease of the holes nucleation rate for the long annealing times. We related this decrease to the role of grain boundaries and triple junctions in the nucleation of holes, and the grain growth in the film during annealing. Every expanding hole was partially surrounded by the elevated, abnormally large grains, while the remaining part of the hole contacted an unperturbed film of the original thickness. The expansion of the holes occurred predominantly in the direction of the flat film. We formulated a kinetic model of hole expansion based on surface diffusion along the edge of a flat rim in the direction of an abnormal elevated grain.

1. Introduction

Thin metal films deposited on non-wetting inert substrates agglomerate at elevated temperatures well below the melting point of the corresponding metal. The process of film agglomeration, also known as solid-state dewetting, is driven by reduction of total surface and interface energy of system [1], while its kinetics is controlled by self-diffusion on the surface of the metal. The solid-state dewetting begins with the nucleation of the through-holes in the film that expand by the motion of the triple phase (vapor/substrate/film) junctions. The material rejected by the holes commonly accumulates at their rim forming a web-like or branched structure at the intermediate stages of dewetting. In most cases, the process ends with the formation of anisotropic faceted single crystalline particles. Such particles are structurally perfect, and they represent convenient objects for studying the nanoscale plasticity [2,3] and for determining the surface and interface energies [4,5]. The solid-state dewetting becomes an acute problem in the case of ultrathin films, when the continuity and integrity of the film is required. On the other hand, metal film agglomeration can be utilized in the fabrication of micro- and nanoparticle arrays for catalytic growth of carbon nanotubes and semiconductor nanowires [6,7], for sensing [8], and for plasmonic and optical applications [9,10]. The dewetting of bi-layers was recently employed for producing of core-shell metal nanoparticles [11]. The complex interconnected web-like metallic structures formed during intermediate stages of dewetting can serve as electrodes for fuel cells [12]. A number of experimental and theoretical studies of dewetting are available in the literature [1,13–15]. In practical terms, however, the dewetting process still cannot be fully controlled.

Recent studies have demonstrated that intrinsic surface anisotropy of metals (both in terms of surface energy and surface diffusivity) plays an important role in solid state dewetting [16–22]. For example, in a series of works on Ni films deposited on MgO substrates, Ye and Thompson showed that the rim retraction rate, rim height, and the shape of the dewetting front are dictated by the crystallographic orientation of the rim [18–20].

In case of polycrystalline thin films an additional complexity is added due to the presence of grain boundaries (GBs), and the grain growth process which proceeds simultaneously with dewetting. The electron backscattered diffraction (EBSD) studies of dewetting of polycrystalline Au film on SiN$_x$ conducted by Müller and Spolenak have shown that the holes protrude along the high angle grain boundaries [23]. The abnormal growth of the grains with the low-index orientation relationship (OR) to the substrate was observed during dewetting of the Pt film on A-plane oriented sapphire substrate [24]. Also, the abnormal grains exhibited faceted shapes, and the rate of hole expansion in their direction was significantly reduced. This was attributed to the local energy minimum of the

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http://dx.doi.org/10.1016/j.actamat.2017.07.057
1359-6454/

corresponding surfaces/interfaces of the abnormal grains. The dewetting behavior of Pt films deposited on yttrium-stabilized zirconia (YSZ) was somewhat different [25]. The growing hillocks were shown to accumulate mass from the adjacent holes with flat rims. The flat hole rims were also found in the *in-situ* experiments on the dewetting of Ag films deposited on amorphous SiO_2 [26], and in the dewetting studies of thin Fe films on sapphire substrates [27], in which the abnormal grain growth and growing hillocks separated from the holes were observed. This is different from the classical kinetic picture of dewetting based on the surface diffusion, and can be understood in terms of additional mass transfer routes, such as GBs and the film-substrate interface [23,27,28].

This variety of the possible kinetic routes of mass transfer, and an important role played by surface/interface energy and diffusivity anisotropies points on the complexity of the dewetting phenomena in polycrystalline thin films. This also means that the dewetting behavior may be very different for different film-substrate couples, or even for different annealing conditions for the same couple. Indeed, Kosinova et al. have demonstrated that the morphologies of the dewetting holes in the Au-sapphire system can be manipulated by changing the annealing atmosphere [29].

In this respect, it should be noted that most of the solid-state dewetting studies of thin polycrystalline metal films reported in the literature were conducted on the face centered cubic (FCC) metals [30]. The general common features of these studies can be summarized as follows:

- Abnormal grain growth occurs in the rim of the expanding dewetting holes. The grain growth in the rim region was observed for a number of different substrates, including the self-assembling organic monolayers [31];
- The nucleation of a hole is a rare event not directly related to the GB grooving. The nucleation of holes was related to the random impurities (leaving a characteristic central feature within the holes [1]), agglomeration of excess vacancies [32], and to the pre-existing pores at the metal-substrate interface [33,34]. Only in few cases a direct nucleation at the GB triple junctions was observed [35]. The difficulty of hole nucleation in the FCC metals can be attributed to their relatively high surface energy anisotropy capable of slowing down or preventing the GB grooving process [36].

The aim of the present work was to understand whether the initial stages of dewetting of the thin film of a body centered cubic (BCC) metal are different from those of its FCC counterparts. We have selected the Mo-sapphire couple for this study. In practical terms, the Mo/Al_2O_3 composites are considered as very attractive candidates for high temperature applications because of the very close linear thermal expansion coefficients and elastic moduli of the components [37,38]. The microstructure, thermal and mechanical properties of the Mo/Al_2O_3 composites were investigated in a number of works, yet to the best of our knowledge there are no reports in the literature on the agglomeration behavior of thin Mo films on sapphire. We sought to fill this gap by investigating the solid state dewetting of thin films of Mo (which is a typical refractory BCC metal) on sapphire. Knowing the thermal stability and adhesion in the Mo-sapphire system obtained in dewetting studies can be useful for a number of practical applications.

2. Experimental

Molybdenum film of 20 nm in thickness was deposited with the aid of magnetron sputtering on the *c*-plane oriented polished sapphire substrate. The substrate wafers was ultrasonically cleaned with acetone, ethanol, isopropanol and de-ionized water prior to the deposition. The deposition was performed in the radio-frequency magnetron sputtering apparatus (Von Ardenne) employing Mo target of 99.9 wt. % purity (Kurt J. Lesker). After the film deposition micro-indentation marks mapping was made by Vickers micro hardness indenter to enable tracking the same areas of the film after consecutive heat treatments.

The thermal treatments at 940 °C were performed in rapid thermal annealing (RTA) furnace (ULVAC Mila 5000) in the constant flow of $Ar + 10\%H_2$ ultra-high purity (UHP) gas preventing the oxidation and causing a reduction of native oxide film formed during samples manipulation in air. The sample was placed in the quartz boat on the clean sapphire wafer and annealed for time intervals ranging from 15 min at the initial stages of dewetting up to 60 min for last two heat treatments; the total time of interrupted annealing of the sample being 300 min. The heating rate to the target temperature was set to 10 °C/s after 1 min hold at 120 °C. Additionally, fully agglomerated films were obtained by annealing the films in the same $Ar + 10\%H_2$ environment at 1380 °C for 24 h in the high temperature tube furnace (MTI GSL - 1500x − OTF) equipped with the mullite tube. After each treatment the film surface topography was measured in tapping mode employing XE-70 atomic force microscope (AFM) of Park Systems Corp. with Si probes (NSC30, NT-NDT). The topography evolution of two different areas of the film ("Site 1" and "Site 2") was tracked. Additionally, the samples were examined in a scanning electron microscope (SEM; Zeiss Ultra-Plus FEG-SEM). The texture of the film was examined with the aid of electron backscattering diffraction (EBSD) employing the QUANTAX EBSD system (Bruker) in SEM. The X-ray diffraction patterns (XRD; Rigaku SmartLab) were obtained for the as deposited and fully agglomerated films using Cu $K\alpha$ radiation in a parallel beam configuration. The in-plane pole-figure (PF) for the fully agglomerated sample was obtained with the slit collimation.

3. Results

The evolution of the Mo film topography at the Site 1 during consecutive heat treatments is shown in Fig. 1. Similar dewetting morphologies were observed at the Site 2 (see Fig. S1 of the Supplementary Material). One can see that new holes nucleate during consecutive annealings simultaneously with the growth of their previously nucleated counterparts. The initial holes in the film are surrounded by one or more grains which are higher and larger than their neighbors located farther from the hole (Fig. 2); However, in most cases a certain portion of the hole rim contacts seemingly unperturbed, flat Mo film, with the grain size and shape near these sections of the rim being similar to those in the unperturbed parts of the film.

The nucleation of new holes occurs both at the random locations in the film and on the opposite side of the large grains adjacent to the growing holes which nucleated earlier. The dependencies of the total amount of holes on the cumulative annealing time for both studied sites are presented in Fig. 3(a), together with the least-square fit curve based on the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation with the constant nucleation rate of holes (see Section 4.1).

Expansion of the holes continues with time and additional large elevated grains appear at the hole edge. Developed holes have a pronounced faceted shape. The retraction rate of the rims bounded by elevated faceted grains is significantly slower than that of flat edges. The expansion of the holes slows down when they become surrounded by large faceted grains from all sides. The dependence of the area of four distinct individual holes on the annealing time shown in Fig. 3 (b) is representative of all other holes. The behavior of new holes that nucleate at different stages of the experiment is very similar to the behavior of the initial holes.