PIT INITIATION IN AlO_x/Al THIN FILMS

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ABSTRACT

The electrochemical responses of AlO_x/Al thin films have been investigated as a function of film growth conditions which produce films with different grain orientation, size and morphology. Films with smooth, 150 nm diameter, randomly oriented grains show a higher pitting potential and lower passive current than those films with large grain-boundary grooving from a mixture of smooth micron-sized, (200)-oriented grains and 300-500 nm diameter, (220)-oriented grains. These results suggest that surface roughness from grain-boundary grooving affects the pitting resistance more strongly than does the grain boundary density.

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INTRODUCTION

Local corrosion in passive materials has been investigated extensively, and significant understanding has been gained in the role of passivity and the effects of both external and internal parameters on pit propagation (1, 2, 3). However, systematic studies on localized corrosion initiation in Al and Al alloys are still lacking, primarily due to the complexity of the system. Fundamental questions such as why corrosion initiation is localized and what are the initiation mechanisms still remain unanswered. Microstructural heterogeneities and oxide film defects are often invoked as key factors governing pit initiation (1, 2, 3). However, bulk metal and metal alloys typically contain a wide variety of poorly characterized defects, and elucidation of a general pit initiation mechanism is difficult. In order to isolate mechanisms responsible for pit initiation in the AlO_x/Al system and in Al alloys, we use thin film deposition combined with lithographic techniques to prepare specific defect types (4) in a controlled manner, such that the defect and its role in pit initiation may be identified. These defect structures are fabricated on deposited Al thin films, and thus it is important to understand the pitting response of these thin-film templates without prepared defects. In this paper, as an initial step, we determine the effects of film grain size, orientation, and morphology on the pitting potential and passive current of micron thick Al films prepared at different substrate temperatures and growth rates.

EXPERIMENTAL

The Al films were deposited by electron-beam evaporation from 99.9999% pure Al onto Si (100) substrates in an ultra-high vacuum chamber with background pressure $< 3 \times 10^{-8}$ Torr (5). Prior to film deposition, the Si substrate was cleaned with low-particulate, electronic grade acetone and isopropyl alcohol in order to remove residual contaminants. The deposition rate was varied between 0.1 and 1.0 nm/s at substrate temperatures ranging from ambient up to 300 °C, allowing control of the resulting grain size, orientation and morphology. The passive oxide was grown by exposing the surface to laboratory atmosphere.

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Grain size and roughness were determined by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), respectively. Grain orientation was determined by x-ray diffraction measurements on a four-circle diffractometer using Cu K α radiation from a fixed anode source. Standard θ - 2θ scans were used to characterize films with random grain orientation and pole figure measurements were used to study preferential grain orientation.

The electrochemical response of the samples was measured using potentiodynamic polarization tests. All tests were performed in a de-aerated 0.05 M NaCl solution at ambient temperature. A three electrode configuration was used in a vertically oriented Plexiglas test cell for all electrochemical testing (a counter electrode consisted of platinized niobium mesh, a primary Ag/AgCl reference electrode consisting of a chloridized Ag wire, and a secondary calomel reference electrode). The working electrode was masked to an approximate area of 0.3-0.5 cm² using micro-stop lacquer that served to prevent crevice corrosion. The exposed area was measured optically using a digital image processing system. The potential of the Ag/AgCl electrode was approximately 0.060 V vs. a saturated calomel electrode. The applied potential was ramped at 0.1667 mV/sec in the anodic direction starting from -1 V (vs. Ag/AgCl electrode). All the pitting potentials reported in this work are referenced to the Ag/AgCl electrode. In this work, the pitting potential is defined as the potential where the anodic current density increase is greater than one order of magnitude as a result of a stepped-potential increase of 0.0025 mV.

RESULTS AND DISCUSSION

The microstructure of electron-beam evaporated Al films is strongly dependent upon the growth temperature and the growth rate. X-ray diffraction measurements show that the Al film on Si(100) has randomly oriented grains at ambient growth temperatures, while at 100 °C and 200 °C, a mixture of (200) and (220) oriented Al grains are formed. At 100 °C, (200) oriented grains dominate the microstructure, while at 200 °C (220) grains dominate. Fig. 1 displays SEM images of the films deposited at two different conditions: (a) 0.1 nm/s, ambient temperature and (b) 1.0 nm/s, 100 °C. These images clearly show that film (a) has a smooth surface with 150 nm-sized randomly oriented grains, and film (b) has smooth 3-10 μ m (200) grains mixed with 300-500 nm (220) grains. Many of the grain boundaries between the (200) and (220) grains of Fig. 1b show deep trench-like structures separating the grains, whereas these deep trench-like structures are absent for the smaller, randomly oriented grains shown in Fig. 1a.

The root-mean-squared (RMS) roughness of these films was measured by AFM as shown in Fig. 2. The 150 nm randomly oriented grains in (a) yield a 7.4 nm RMS roughness for the film, while the RMS roughness of the (200) and (220) grains in film (b) are 2.0 nm and 8.0 nm, respectively. Further, the grain-boundary grooving between the (200) and (220) grains of film (b) was measured to be ~150 nm wide and ~30.0 nm deep. These trench-like grain boundaries between the larger grains are the dominant surface structure observed, and these grooves are much larger than the surface roughness of the individual grains and also much larger than the surface roughness of the smaller-grain film (a).

Electrochemical testing of these two Al films shows the profound effect of Al microstructure, grain size, and surface morphology on the pit initiation characteristics. Anodic polarization measurements of the two films are displayed in Fig. 3. Film (a) with smooth, randomly oriented, 150 nm size grains has a pitting potential of -0.195 V and a passive current density of 1×10^{-6} A/cm². Film (b), which contains (200) oriented grains

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mixed with (220) oriented grains and exhibits grain-boundary grooving, has a much lower pitting potential and higher passive current; -0.586 V and 2×10^{-5} A/cm². We also observe a high frequency current oscillation for film (b) below the pitting potential. Similar current oscillations before stable pit formation have also been observed for bulk Al (6) and have been explained by repeated breakdown-repair events of the passive oxide.

Based on the higher pitting resistance observed for the film with randomly oriented smaller grains (and thus higher grain-boundary density), we suggest that the roughness of grain boundaries is responsible for higher pitting susceptibility rather than grain-boundary density or grain size. The (200)/(220) grain-boundary grooves may have a higher defect density, or the geometry of the trench may produce stresses in the oxide and allow breakdown at highly curved sites (7), resulting easier pit initiation than on the smooth, small-grain random orientation film. Cyclic activation-repassivation observed below the pitting potential for the film with the mixture of (200) and (220) grains may occur because the pit size is not large enough for continued growth (8). Absence of the trench mediated pit initiation in the film with small smooth grains might be one of the reasons for the absence of significant current fluctuation below the pitting potential for the smooth film.

SUMMARY

Two types of Al films were prepared under different conditions and their electrochemical responses were measured. Films with smooth, 150 nm randomly oriented grains have a higher pitting potential and lower passive current than films with a mixture of 3-10 μ m size smooth (200)-oriented grains and 300-500 nm size (220)-oriented grains, which exhibit deep grain-boundary grooving between the (200) and (220) grains. These results indicate that film roughness from grain-boundary grooving has a stronger effect on pitting resistance than grain boundary density.

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(a) 150 nm grain size
random orientation

(b) 3-10 μm grain size
mixed (200) & (220) orientation

Fig.1 SEM images of Al films grown at (a) 0.1 nm/s and ambient temperature and (b) 1.0 nm/s and 100 °C.

(a) 0.1 nm/s, Ambient T
Random

(b) 1 nm/s, 100°C
(200) + (220)

Fig. 2 AFM image of Al films grown at (a) 0.1 nm/s and ambient and (b) 1.0 nm/s and 100 °C.

Fig.3 Anodic polarization curves of Al films with (a) 150 nm, randomly oriented grains and (b) 3-10 μm (200) grains mixed with 300-500 nm (220) grains