Exploring the relationship of morphology and structure to pit initiation in Cl-implanted Al thin films

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Although it is well known that the presence of chloride in an electrolyte can initiate pitting in passive metals, the precise mechanisms responsible for pit initiation are still not well understood. In particular, several parameters required for pit initiation are currently unknown. These include the local Cl concentration, the critical location either at the surface, within the oxide or at the metal-oxide interface, and the nature of the bonding between Cl and the passive film. One approach that allows control of the concentration, location and source of Cl in the system is to use ion implantation.

This technique has been applied to the passive aluminum thin film system (1-3). When the implanted films are polarized in a 50 mM sulfate solution, pitting is only observed when the Cl concentration at the oxide - metal interface exceeds 1 – 3 atomic percent (3). This result suggests there is a critical Cl concentration for pit nucleation. Further insight as to the pitting mechanisms can be gained by characterizing the film morphology, structure and Cl distribution resulting from the ion implantation as the critical concentration is reached.

We have used atomic force microscopy to characterize the film morphology as a function of Cl implant fluence from 1 – 7 x 10^{16} Cl/cm^2, which spans the range of Cl concentrations required to initiate pitting in the sulfate solution. The atomic force microscope (AFM) image shown in Figure 1 is taken from an aluminum thin film sample prior to Cl ion implantation. Figure 2 shows the morphology resulting from a Cl implantation fluence of 3 x 10^{16}/cm^2, which produces a Cl concentration that is just above the threshold for pit initiation in a sulfate solution. The implantation results in clearly defined morphological domains that range in size from that of a single grain (in the non-implanted sample) to that of multiple grains. Further changes in morphology upon polarization towards pitting will be explored, in order to investigate the relationship between pit initiation and surface morphology. The film structure and Cl distribution will be investigated using analytical transmission electron microscopy in order to better understand the role of a critical Cl concentration for pit initiation relative to the role of implant damage in these samples.

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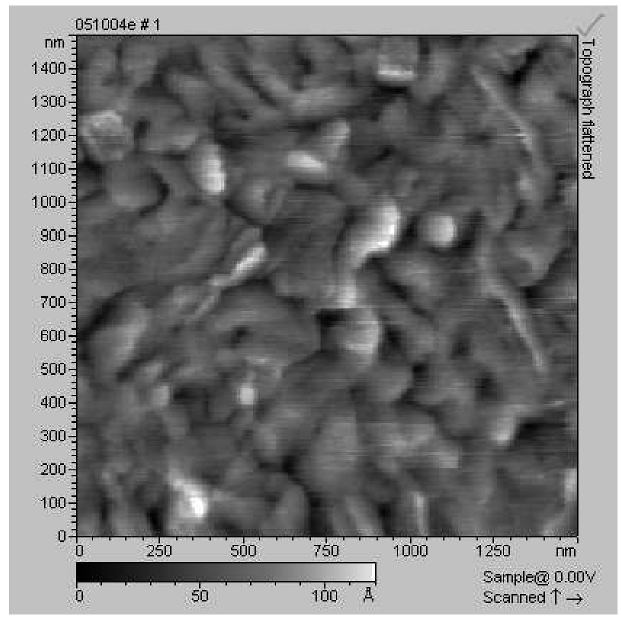

Fig. 1 AFM image of an evaporated aluminum thin film on a SiO2 coated Si substrate prior to Cl implantation.

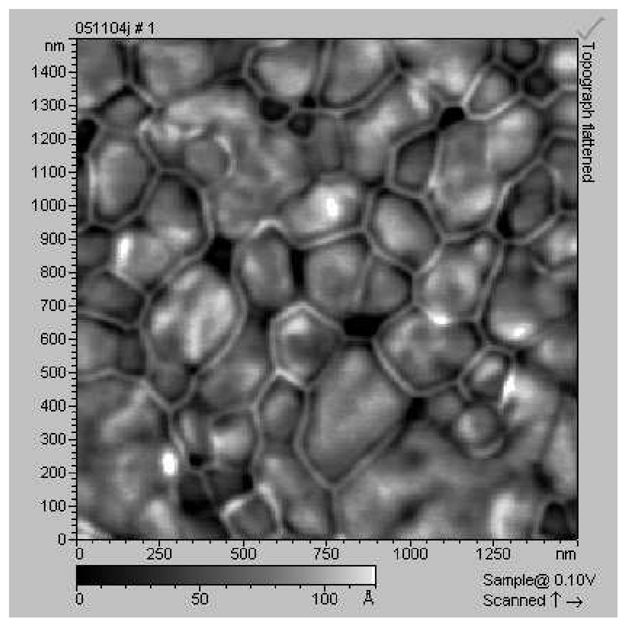

Fig. 2 AFM image of the film shown in Fig 1 following a Cl implantation fluence of 3 x 10^{16}/cm^2.

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