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Effect of Vacuum System Base Pressure on Corrosion Resistance of Sputtered Al Thin Films

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Corrosion of thin film metal samples deposited by sputter deposition or evaporation has attracted considerable attention because of the technological applications of thin films and also the opportunities provided by thin films for studying the pitting phenomenon. Many papers have reported an increased corrosion resistance of thin films relative to bulk alloy counterparts, often expressed as an increase in the pitting potential. Other researchers have found pitting potentials for thin films to be similar to bulk alloys of a similar composition.

Many different reasons for the improved corrosion resistance of thin films have been offered including reduced grain size or improved homogeneity of the microstructure. The hypothesis of this study is that the corrosion resistance of metallic thin film samples can be strongly influenced by the base pressure of the vacuum system used in the deposition process. For base pressures above about 10^{-7} Torr, incorporation of water or oxygen from the residual gas in the chamber can alter the properties of the material and improve the corrosion performance relative to bulk Al samples. The objective is to understand what properties are changed and how they affect the corrosion performance.

Samples were sputter deposited from a 99.99% Al target following evacuation of the chamber to different base pressures ranging from 9×10^{-8} to 5×10^{-6} Torr. A residual gas analyzer was used to evaluate the base vacuum composition. Then high purity (99.999%) argon gas at a flow rate of 20.0 sccm was introduced into the chamber, where a pressure of 1×10^{-3} Torr was achieved during deposition. Metal films approximately 100 nm in thickness were deposited onto ultra-clean glass microscope slides. The as-deposited samples were evaluated by potentiodynamic polarization in 0.1 M NaCl, x-ray photoelectron spectroscopy, transmission electron microscopy with energy dispersive spectroscopy, sheet resistance measurements, and thin film pit growth measurements by optical analysis [1].

A remarkable increase in the pitting potential was observed with increasing system base pressure. Average values of pitting potential were -510 ± 140 mV SCE and +290 ± 40 mV SCE for 9×10^{-8} Torr and 5×10^{-6} Torr, respectively. The sheet resistivity also increased over the same range of base pressure from 480 ± 8 to 630 ± 8 mΩ/square. TEM/EDS analysis of the films found an increase in the oxygen content. Over the range of base pressure the O/Al signal ratio increased from 0.024 ± 0.016 to 0.11 ± 0.06. The RGA analysis indicated that water vapor constituted a large fraction of the residual gas in the vacuum and so the water vapor pressure increased with the base pressure.

Thin film pit growth experiments were performed to assess the pit polarization curve by determining the pit perimeter growth rate as a function of potential. Despite the large difference in pitting potential, the pit polarization curves and repassivation potentials were only slightly offset to more noble potentials as the base pressure during deposition increased. This suggests that the change in pitting potential is not controlled by pit growth considerations.

XPS analysis was performed on as-deposited films and the core line of Al 2p was investigated in detail. The height of the Al(0) peak from the underlying metal substrate decreased as the base pressure increased, as indicated by the ratio of Al(III)/Al(0) peak height increasing from 1.34 to 1.76 over the range of base pressure.

The results suggest that water vapor in the base vacuum of a sputtering system can react with deposited metal during the deposition process to change the properties of the film. A small increase in the oxygen content results in a large increase in the pitting potential of the deposited film, apparently by creating a thicker and more protective oxide layer upon exposure to the ambient environment.

Reference

1. G.S. Frankel, *Corros. Sci.,* 30 (1990) 1203-1218.