Etch Tunnels in Aluminum

R. S. Alwitt[1], K. R. Hebert[2], and T. Makino[3]

[1]Boundary Technologies, Inc., PO Box 622, Northbrook IL 60065-0622
[2]Department of Chemical Engineering, Iowa State University, Ames, Iowa 50011
[3]Chemi-Con Materials Corp., 366 Lexington Drive, Buffalo Grove, IL 60089

This presentation is a review the technology and science of tunnel etching of Al. This subject was last reviewed in the U.S.A. in 1987 [1] and much has been learned since then. Basic studies of tunnel etching have recently made clear that the same fundamental surface processes occur during tunnel etching as for pitting corrosion of aluminum, so this is an appropriate subject for this symposium on corrosion science.

Electroetching of Al to make capacitor foil began about fifty years ago. Anodic dissolution in hot chloride solution produces a dense array of microscopic tunnels. Tunnel etching of 4N purity Al foil enhances surface area by as much as 25x and, after depositing anodic oxide dielectric, this material is used as the anode in electrolytic capacitors. Tunnels are typically 1 μm wide, 40-50 μm long and with density $>10^7$ cm^{-2}. A tunnel initiates when the four sidewalls of a growing half-cubic pit passivate while the bottom continues to dissolve. Tunnel surfaces are (100) planes and the tunnel propagates in the <100> direction. A tunnel results from passivation of sidewalls as the active tip recedes from the surface. Tunnels grow at a constant rate that increases with temperature. At 70C, a typical etch temperature, the growth rate is 2 μms^{-1}, or 6Acm^{-2} [2]. The precursor pits grow at the same rate as the tunnels [3]. The process is under ohmic control, the active surface is at the repassivation potential, E_r, and the active area changes with applied current to maintain a fixed specific current density for anodic dissolution.

Technology

Thousands of square meters of foil are etched worldwide in large-scale continuous processes. The starting material is highly engineered with regard to grain orientation, surface condition and purity. Rolling and annealing conditions are chosen to give a foil surface that is predominantly [100] orientation, so etch tunnels will propagate normal to this surface. Annealing is done in inert atmosphere to control surface oxide. Total impurities is less than 100 ppm, and the amount of certain elements such as Cu and Pb is carefully maintained. For Pb, the bulk concentration is near 1 ppm but during annealing these atoms diffuse to the surface, just under the oxide, to make a layer several orders higher in Pb content. This has an important effect on tunnel initiation.

With suitable process conditions a truly random distributions of tunnels can be produced. The capacitance of a tunnel array with a certain thickness of oxide dielectric can be accurately modeled [4]. Then optimum tunnel dimensions can be defined for maximum capacitance and the challenge is to find process conditions to make that distribution.

Science

The simple tunnel geometry and one-dimensional dissolution process make it possible to model transport and potential profiles in the tunnel, and calculate concentrations and potential at the dissolving tip [5].

From SEM examination of oxide replicas of etched substrates, precise determination is made of tunnel growth rate and hence tip current density, as well as dimensional changes of features on the dissolving surface caused by imposed experimental protocols, e.g., step change in applied current. Hebert and co-workers used these tools to extract information about the dissolution and passivation reactions [6-10]. Current step reduction causes nearly immediate reduction in active area accompanied by a sharp potential decrease of ~100 μs duration. A current pulse following the step reduction causes an anodic transient of similar duration but with no change in active area. From current balances over the transient, the potential dependence of the passivation rate (cathodic transient) [10] and the faradaic current for metal dissolution (anodic transient) [9] were obtained. The dissolution current-potential relation follows Tafel behavior. Pits grown at short etch times exhibit the same passivation behavior and obey the same potential-current relation as tunnels. Moreover, pit growth at 25C follows the same dissolution kinetics [9].

Mechanisms of Passivation and Dissolution

The active surface is covered with an adsorbed Cl$^-$ layer. At E_r dissolution occurs through the Cl$^-$ layer at a rate that depends only on temperature, and the dissolution current is controlled by increase or decrease (passivation) of active area. Passivation is initiated by replacement of adsorbed Cl$^-$ with adsorbed water. Subsequent changes in these surface regions produce a stable oxide. The rate-determining step for passivation is desorption of Cl$^-$. At potentials up to ~100 mV anodic to E_r the dissolution process is controlled by a surface reaction following Tafel kinetics that supports currents >30 Acm^{-2}. In tunnel etching and in pitting corrosion the potential stabilizes at E_r and dissolving areas adjust in number and size to support the required dissolution current. Small adjustments of potential in the vicinity of E_r maintain the dissolution current density by promoting or inhibiting passivation at the edges of active areas. The AlCl$_3$ concentration in a tunnel is high, but there is no evidence for a salt film on active surfaces during tunnel growth.

References
1. R.S. Alwitt, T.R. Beck, and K.R. Hebert, in *Advances in Localized Corrosion*, H.S. Isaacs *et al* Editors, p. 145, NACE, Houston, TX (1990).
2. R.S. Alwitt, H. Uchi, T.R. Beck, and R.C. Alkire, *J. Electrochem. Soc.* **131**, 13 1984).
3. B.J. Wiersma and K.R. Hebert, *ibid.* **138**, 48 (1991).
4. D. G.W. Goad and H. Uchi, *J. Appl, Electrochem.*, **30**, 285 (2000).
5. K.R. Hebert and R.C. Alkire, *J. Electrochem. Soc.*, **135**, 2146 (1988).
6. B.J. Wiersma, Y. Tak, and K.R. Hebert, *ibid.*, **137**, 371 (1990).
7. Y. Tak, E.R. Henderson, and K.R. Hebert, *ibid.*, **141**, 1446 (1994).
8. Y. Tak and K.R. Hebert, *op. cit.*, 1453.
9. Y. Tak, N. Sinha, and K.R. Hebert, *ibid.*, **147**, 4103 (2000).
10. N. Sinha and K.R. Hebert, *op. cit.*, 4111.