Electrodissolution of aluminium thin film microband electrodes

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This paper discusses the electrodissolution of aluminium thin films as microband electrodes (length = $5 \times 10^{-3}$ m) in terms of mass transfer determined by voltammetry and a.c.-impedance techniques as a function of bandwidth (20 to 2000 nm) in 0.1 M NaOH solution. The anodic polarization curves of the aluminium microband electrodes show that current density is enhanced with decreasing bandwidth. The ac impedance response suggests that a steady-state diffusion layer appears the more markedly, the smaller the bandwidth. The anodic polarization curves are analysed on the basis of the combined Butler–Volmer high field approximation and the semi-cylindrical diffusion field approximation. As a result of the analysis, the electrodissolution proceeds by a mixed kinetic-mass transfer controlled reaction. The analysis also makes it possible to distinguish the semi-cylindrical diffusive mass transfer contribution to the electrodissolution from the kinetic contribution, i.e., mass transfer index linearly diminishes with decreasing bandwidth. The increased current density is attributable to the decreased mass transfer contribution, i.e., the more predominant semi-cylindrical diffusive mass transfer as compared to laminar diffusive mass transfer.

Nomenclature

- $k_a$: anodic kinetic constant
- $k_c$: cathodic kinetic constant
- $F$: Faraday constant
- $\alpha_a$: kinetic transfer coefficient for anodic reaction
- $\alpha_c$: kinetic transfer coefficient for cathodic reaction
- $c_s$: surface concentration
- $V$: anodic polarization
- $D$: diffusion coefficient
- $d$: diffusion layer thickness
- $z$: number of electrons transferred
- $l$: length of microband electrode
- $w$: bandwidth of microband electrode
- $r$: radius of cylinder
- $\nu$: rate or corrosion rate of the aluminium thin film on a microscopic scale.

1. Introduction

Aluminium based thin films are commonly used as electronic conductors on silicon integrated circuits (IC) in microelectronic structures. The susceptibility to corrosion in aggressive environments determines the life time of the IC system. The electrodissolution of aluminium based alloys has been extensively studied in various aqueous electrolytes for life time prediction in practical systems using a macroelectrode. In general, dissolution rate on aluminium alloy macroelectrodes is largely controlled by the rate at which dissolved ions are removed from the electrode surface by convection and diffusion [1–4]. A question arises as to how the electrodissolution of aluminium alloys proceeds from the electrode surface on a microscopic scale. The diffusional flux to the microelectrode for a cathodic process is greatly enhanced as compared to the macroelectrode, since the contribution of two- or three-dimensional diffusion, rather than linear diffusion, is considerably enhanced with decreasing dimension of the microelectrode [5–8].

Therefore it is expected that results for macroelectrodes do not give information about dissolution rate or corrosion rate of the aluminium thin film on a microscopic scale. Considering that electrode kinetics are independent of specimen dimension, it is possible to distinguish the mass transfer from the kinetic contribution to the anodic dissolution current of aluminium thin films by using microelectrodes. The present paper is aimed at examining how diffusional mass transfer from a microband aluminium electrode, as a function of bandwidth, affects the anodic dissolution of aluminium thin films in alkaline aqueous solution. For this purpose, potentiodynamic polarization and ac-impedance measurements were performed on aluminium microband electrodes. The experimental results obtained were analyzed on the basis of the combined Butler–Volmer high field approximation and semi-cylindrical diffusion field approximation.

2. Experimental details

Aluminium thin films were coated onto an insulating silicon oxide to thicknesses ranging from 20 to 2000 nm by a conventional sputtering technique. The Al/silicon oxide was then sealed in polyethylene resin. The assembly was polished to expose the cross...
section of the aluminium films. The specimen was ground with successively finer silicon carbide paper, ending with 1200 grit and was finally polished with 0.05 μm Al₂O₃ powder on wet cloth. The edge of this assembly was employed as an aluminium microband electrode, which was characterized by a microscopic bandwidth (20–2000 nm) and a macroscopic length of 0.5 cm (Fig. 1).

Electrochemical experiments were conducted in a EG&G Model KO 235 flat cell. The working electrode was the aluminium microband electrode, and a platinum mesh and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The electrolyte was 0.1 M NaOH solution, previously deaerated for 24 h and agitated by bubbling with purified nitrogen throughout the experiments.

Potentiodynamic polarization experiments were conducted on aluminium microband electrode at a scan rate of 0.2 mV s⁻¹ in the potential range -1400 to -900 mV vs SCE after a 2 h exposure at open circuit in order to activate the specimen surface, using an EG&G Model 273 potentiostat. The open circuit potential was found to be about -1040 mV vs SCE.

Electrochemical impedance spectroscopy (EIS) was performed on the aluminium microband electrode with a Solartron model 1255 frequency response analyser in conjunction with a Solartron model 1286 potentiostat by superimposing an a.c. voltage of 5 mV amplitude on a dc potential over the frequency range 10⁻² to 10⁴ Hz. The dc potentials applied to the specimen were an anodic potential of -900 mV vs SCE and a cathodic potential of -1350 mV vs SCE.

3. Theoretical background

When aluminium is exposed to an aqueous electrolyte, the hydrated aluminium ion, Al(H₂O)₆³⁺, is rapidly formed, equilibrium being achieved in about 1 μs [9].

\[
\text{Al} + 6\text{H}_2\text{O} = \text{Al} (\text{H}_2\text{O})_6^{3+} + 3\text{e}^-
\]  

(1)

The current density for aluminium dissolution, \(i\), is described by the Butler-Volmer relationship [10]

\[
i = k_a F \exp \left( \frac{\alpha a F V}{RT} \right) - k_c c^e \exp \left( -\frac{\alpha c F V}{RT} \right)
\]  

(2)

The steady state flux of Al(H₂O)₆³⁺, \(n\), through a diffusion layer from the electrode may be expressed as

\[
n = Dc^e/d
\]  

(3)

From Equations 2 and 3, and using

\[
i = \frac{k_a F \exp \left( \alpha a F V/RT \right)}{1 + \frac{k_a}{k_c}d \exp \left( -\alpha c F V/RT \right)}
\]  

(5)

Equation 5 describes the current–potential behaviour for electrode dissolution of aluminium and provides two limiting cases concerning the kinetic and mass transfer effects. First, when the second term in the denominator of Equation 5 is much smaller than the first, \(i\) is given by

\[
i = k_a F \exp \left( \frac{\alpha a F V}{RT} \right)
\]  

(6)

This represents the kinetic contribution to the current density in the absence of mass transfer effects. Secondly, in the case where the second term is much larger than the first, \(i\) is given by

\[
i = k_a F d \exp \left[ \frac{\alpha a F V}{RT} \right]
\]  

(7)

Equation 7 describes the limiting behaviour when the dissolution is mass transfer controlled. It can be therefore said that the second term in the denominator of Equation 5 gives an indication of the extent of the mass transfer effect for a mixed kinetic–mass transfer controlled reaction and furthermore permits separation between kinetic and mass transfer effects. An increase in the mass transfer effect reduces the current density.

Fig. 1. Schematic representation of aluminium microband electrodes.

Fig. 2. Anodic polarization of aluminium microband electrodes with different bandwidths in 0.1 M NaOH solution. Bandwidth: (●) 20, (■) 80, (▲) 160, and (○) 500, (□) 2000 nm. Corrosion potential = -1040 mV vs SCE.