

# Anodisation of Thin Film Aluminum.

C Douglas<sup>†</sup>, P Evans<sup>\*†</sup> and R.J. Pollard<sup>\*†</sup>

\* Nanotec Northern Ireland, Belfast, UK

<sup>†</sup> Queen's University of Belfast, Belfast BT7 1NN, r.pollard@qub.ac.uk

## ABSTRACT

We have investigated the single step anodisation of aluminum films in sulfuric, oxalic and phosphoric acid. In general increasing anodisation voltage is found to lead to increasing volume expansion, for a given acid. It is also shown that it is important to match the anodisation conditions to the electrolyte to maximize the ordering for a given pore size. Preliminary work on the electrodeposition of magnetic materials into the pores has also been carried out.

**Keywords:** porous alumina, nanopores, anodisation, nanowires

## 1 INTRODUCTION

It has been known since the fifties that anodisation of aluminum leads to a porous aluminum oxide structure [1]. More recently it has been shown that a two step anodisation process leads to greater pore ordering [2]. As conventional lithographic techniques reach their lower limit in terms of feature size, there has been increased interest in anodic alumina as a quick and economic method for producing nanostructured material over a large area. Here we have examined the single step anodisation of Al films grown by sputter deposition.

## 2 EXPERIMENTAL

Aluminium films were grown on glass substrates by DC magnetron sputter deposition. Anodisation was carried out at constant voltage with a platinum counter electrode. The electrolyte was kept cooled and the temperature monitored throughout the anodisation process. Cross-sections were prepared for transmission electron microscopy (TEM) using a Philips focused ion beam system.

## 3 RESULTS

### 3.1 Growth of porous alumina

Figure 1 shows current-time curves for the anodisation of a 300nm Al film on glass in (a) 0.3M Sulfuric (b) 0.3M Oxalic acid and (c) 10% phosphoric acid under typical conditions. It can be seen that the curves in sulphuric and oxalic acid show the same features although the time scale is different. **Stage I** is a decrease in the current until a minimum is reached at which point it increases (**stage II**) to a plateau (**stage III**). Finally the current decreases, (**stage IV**) to the final small residual value. The current in phosphoric acid shows only a decrease to a plateau and then the final decrease.

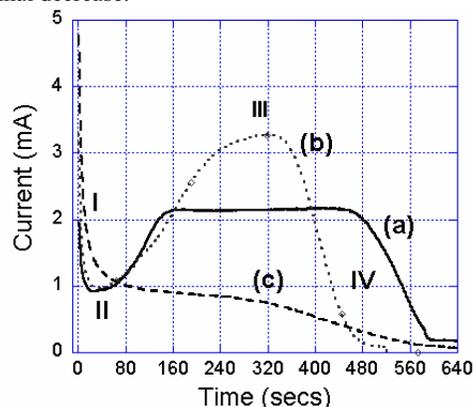


Figure 1: Current time curves for anodisation for (a) 0.3m Sulfuric acid 20V (b) 0.3m Oxalic acid 40V (c) 10% phosphoric acid 100V

TEM cross-sections were prepared at the various stages of growth to help explain these I-t curves. The initial large current is due the initial formation of an aluminium oxide layer, the current decreases as this layer is more resistive than aluminium. The pores start to form and the current increases due to dissolution of the alumina (stage II). The thickness of this initial oxide layer is ~88nm for 10% phosphoric acid (60V), 74nm for oxalic (60V) and 21nm for sulfuric(15V). A plateau is reached when the dissolution of the alumina to form the pores is in equilibrium with the growth of the aluminium oxide in front of the advancing pores. Finally, when all the aluminium has been used-up the current drops, leaving a 'barrier layer' of oxide at the

bottom of the pores. This final barrier layer is 16nm thick for film anodised in sulfuric acid (15V), 42nm for oxalic acid (60V) and 89nm for phosphoric (60V), following the same trend as the initial oxide layer prior to pore growth. Figure 2 shows a TEM cross-section of a film anodised in 0.3M oxalic acid (60V 4°C) where the barrier layer can be clearly seen. Figure 3 shows the surface of a film anodised in 0.3M sulfuric acid (20V, 3°C) after milling.

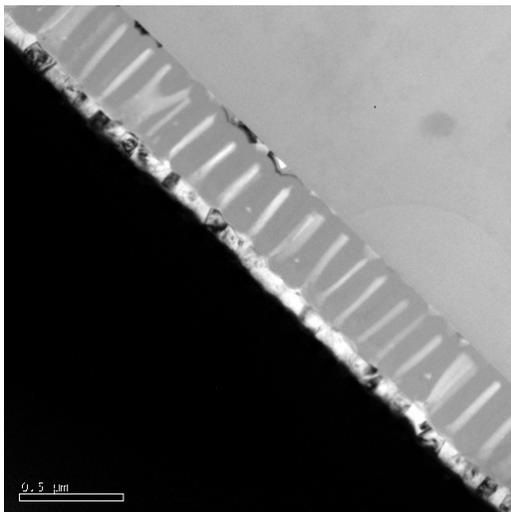


Figure 2: TEM cross-section of porous alumina anodised in 0.3M Oxalic acid at 60V (40 nm pores). The barrier layer at the bottom of each pore can be clearly seen.

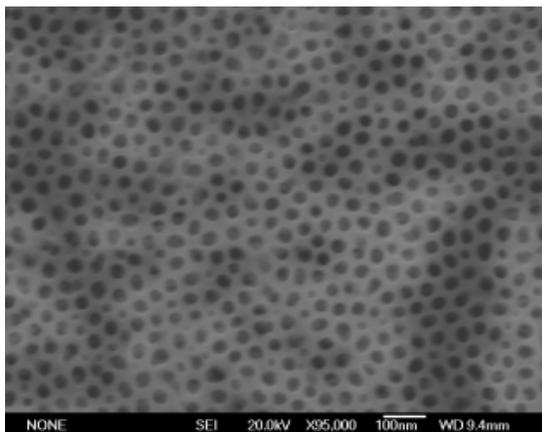


Figure 3: SEM of porous alumina anodised in 0.3M sulfuric acid at 20V (15 nm pores).

The growth of the pores in the phosphoric acid is found to proceed in the same way as the other two acids, but the initial minimum in the current-time curve is not seen, possibly due to the greater oxide thickness.

A volume expansion is expected when Al forms  $Al_2O_3$  and is indeed observed in the cross-sections. The volume

expansion is found to show a linear response with applied voltage. The degree of volume expansion is found to be similar for oxalic and phosphoric,  $\sim 1.2$  for an anodisation voltage of 60V and 1.6 for phosphoric at 100V with a similar expansion being predicted for oxalic acid by linear extrapolation from the relationship at lower voltages. The voltage expansion for sulfuric is seen to increase much more rapidly with voltage, 1.2 at 15V and 1.8 at 25V. The mechanical stress from the expansion of the oxide layer is believed to be the result of repulsive forces between neighboring pores during growth that leads to self-organized formation [3]. A moderate expansion of 1.2 is associated with highly ordered growth in oxalic and sulfuric [3]. An expansion of 1.6 at 100 volts phosphoric was obtained for the best-ordered films and this considerable expansion may be allowed due to the slower conversion rate during anodisation. The anodisation rate in phosphoric is three times slower at 100 volts than oxalic at 60 volts and sulfuric at 15 volts, which have lower volume expansions. So it must be the rate rather than the amount of volume expansion when anodising in sulfuric and oxalic that may cause limitations at higher voltages due to the adhesion to the substrate.

### 3.2 Electrodeposition into templates

Electrodeposition is an inexpensive method of producing high quality magnetic material [4]. It differs from vacuum deposition techniques in that the electrical properties of the substrate play an important part in the growth. In order to electrodeposit into the pores a conductive backing layer, such as gold, is needed.  $Ar^+$  ion milling at normal incidence removes the oxide barrier layers at the bottom of the pores and exposes the conductive Au layer. The template can then be electrodeposited onto with the material growing on the conducting gold but not the insulating aluminium oxide. This allows wires with large aspect ratios to be formed.

Figure 4 shows the current time curve for Ni wires grown at  $-1V$  (vs. SCE) from a 0.1M  $NiSO_4$  solution. The alumina template had 40nm pores. There is a large initial current, which decreases as the concentration of ions near the surface of the growing wires decreases until it reaches a steady value governed by diffusion (point 1). When the wires reach the surface of the template there is an increase in current due to the increase in surface area (point 2). Figure 5 shows a cross section of a nanowire stopped shortly after the current dropped to a steady value whilst figure 6 shows what happens if the wires are allowed to grow until they reach the surface.

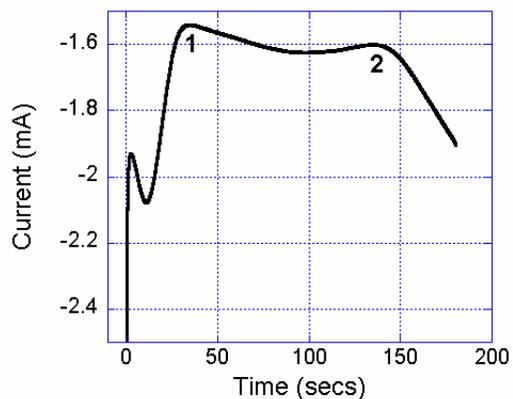


Figure 4: Current vs time for Nickel nanowires grown in 40nm pores (oxalic 60V). Point 2 corresponds to the point the wires reach the surface

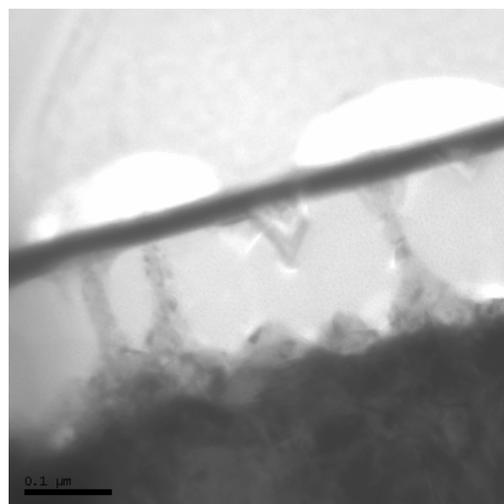


Figure 6 Ni wires electrodeposited in 40nm pores (oxalic 60V). The wires were allowed to reach the surface (point 2 in fig 4) before the growth was stopped

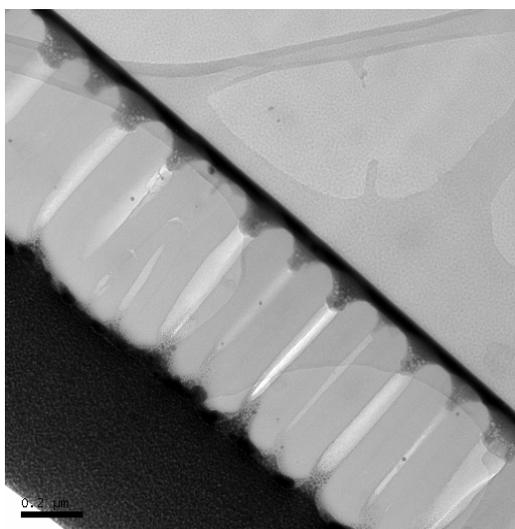


Figure 5 Ni wires electrodeposited in 40nm pores (oxalic 60V). The growth was stopped shortly after the wires started growing (point 1 in fig 4)

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