Nanotemplate alumina films on a silicon substrate fabricated by electrochemistry

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Abstract. The anodization process for the formation of very thin porous alumina films on Si was investigated in detail in this paper. The evolution of current density versus time during anodization was first investigated, and Transmission Electron Microscopy was used to characterize the samples at different anodization times before full Al consumption. Anodization was performed in two different electrolytes and the obtained films were compared.

1. Introduction
Thin anodic alumina films on a silicon substrate are very interesting in many applications, including their use as template for the fabrication of regular arrays of quantum wires or dots [1], as a gate dielectric [2] or as an interlayer gate material. An extensive number of references is found in the literature on thick anodic alumina films on aluminum [3-5] and fewer on Si [6-9] (thickness > 500 nm). However, the fabrication of very thin alumina films on Si by anodization is still an open and challenging subject of research [2, 10]. The conditions of forming very thin anodic alumina films on silicon (thickness below 100 nm), with regular pore arrays, show important differences from those of thicker films, due to the fact that in this case surface phenomena are highly involved.

In this work, we investigated in a systematic way the anodization conditions for the formation of porous anodic alumina films on Si, of thickness below few hundred nanometers, using sulfuric and oxalic acid electrolytes.

2. Experimental results and discussion
The anodization process was first investigated by monitoring the anodization current density versus time and investigating by Transmission Electron Microscopy (TEM) the films fabricated with different anodization times.

2.1. Anodization phases
The current density (J) versus time (t) was monitored during anodization, using an automatic current-time (I-t) sweep controlled by a PC. An example of a typical J-t curve is shown in figure 1. The curve consists of 3 parts: in the first part at the beginning of the process, the current density reaches rapidly a maximum value, and it then decreases also rapidly and it tends to stabilize to a minimum value. This is the first anodization phase. At a certain point of the curve, there is a second increase and a smaller maximum, followed by a decrease with a slightly different (smaller) slope. This is the second anodization phase. The third anodization phase starts with an abrupt decrease of the current, and it...
continues with a slightly decreasing curve with further reduced slope which tends to stabilize just above zero. This is the third anodization phase, during which the film is fully anodized and we stop the anodization process. This behavior was observed in all anodized samples. The first and second phases are in agreement with results in the literature [11] for thicker films, while the step at the beginning of the third phase, observed in all our samples, was not mentioned previously. In order to fully characterize the alumina structure at each phase, three samples were fabricated by anodization of an Al film, 30 nm thick, at different anodization times, corresponding to phase I (sample 1), the beginning of phase II (sample 2) and phase III (sample 3). The J-t curve of sample 3 is illustrated in figure 1. Figs. 2a to c show plan-view TEM images of samples 1 to 3. In all cases the films were anodized in an oxalic acid aqueous solution, 6% in weight, under a constant voltage of 30 V.

![J-t anodization curves for a 30 nm thick Al film anodized in 0.6 M oxalic acid.](image1)

![Plan-view TEM images of samples anodized in oxalic acid for 3 different anodization times, corresponding to parts I, II and III of the anodization curve of figure 1 respectively.](image2)

The first two TEM images were obtained with the electron beam focused at the boundary between the thinnest area of the TEM sample, where only the alumina film is visible, and a thicker area, where the substrate was not fully removed. In figure 2a (sample 1) we see that the alumina film is still compact without pores, while many big crystals are visible underneath, clearly identified in area 2. Diffraction patterns confirmed that these crystals were Al and not alumina crystals. So at this phase, Al is not fully consumed and the pore formation has not started yet. In phase II (sample 2, figure 2b) we see that pore formation was initiated, while the remaining Al layer was thinner (only few Al crystals were seen in area 2). Pore initiation is better illustrated at higher magnification in the inset of figure 2b (area 1 of sample 2). It is clear from this figure that the second current density maximum in the J-t curve corresponds to the initiation of pore formation [11]. During phase III (sample 3, figure 2c) the Al layer is fully consumed and the alumina layer is fully formed, with the pores fully developed. In order to obtain this result the anodization process must be cut when the current density starts to fall to zero with an extremely slow rate. From the usual scalloped appearance of the alumina films on an aluminum substrate, we should expect some remaining Al islands of a conical shape at the interface of alumina with silicon, located at the bents between the pores. These islands are probably consumed at the end of phase II and this is why we observe the third step in the curve. Otherwise, phases II and III should coincide. If we stop anodization when the current density starts to fall to zero (end of phase III), the interface of alumina with Si shows the typical form illustrated in figure 3a, where we identify a void between a thin alumina barrier layer at the bottom of the pore and the silicon substrate [12-13]. The barrier layer is easily dissolved if the sample is immersed in a 5% in weight phosphoric acid aqueous solution for 2-3 minutes and then the pore is connected to the silicon substrate. If we don’t stop anodization on time, then there is an abrupt increase in the current at a certain point of phase III and silicon oxide starts to form at the bottom of the pores, which is rapidly extended to a film underneath alumina (see figure 3b). The nature of this film is further investigated.
2.2. Fully anodized thin porous anodic alumina films on Si in two different electrolytes

In order to compare the influence of the electrolytic solution on the formation of very thin alumina films on Si, we prepared films in two of the most commonly used electrolytes for the fabrication of porous alumina, namely sulfuric and oxalic acid aqueous solutions under constant voltage. The anodization time used corresponded to the end of phase III of the J-t curves. Al films were deposited by e-gun evaporation on a p-type silicon substrate. Two different Al thicknesses were used, 30 and 500 nm. Details on the electrolyte concentration and the voltage used are given in table I [12]. For each electrolyte we used two different anodization conditions, in the range of optimum conditions in the literature for the most homogeneous structures [3-5]. Structural characterization was performed by plan view and cross sectional TEM images and the results on pore and cell diameter as well as on pore density are given in table I. In all cases amorphous porous alumina is obtained, with cylindrical pores, vertical to the silicon substrate, uniformly distributed. An example of plan view TEM images is shown in figure 4.

Table 1. Structural characteristics of films resulting from anodization of Al films of two different thicknesses on Si at different conditions in two different electrolytes.

| Electrochemical Solution | Pore Diameter (average) (nm) | Cell Diameter (average) (nm) | Pore Density (pores/cm²) | Porosity (%) |
|--------------------------|-------------------------------|------------------------------|--------------------------|--------------|
| Al film thickness before anodization: 500 nm |
| Sulfuric Acid (6% v.v. (1 M), 20 V) | 16 | 40 | 8 x 10¹⁰ | 14,5 |
| Sulfuric Acid (2,7% v.v. (0,5 M), 25 V) | 24 | 62 | 4 x 10¹⁰ | 13 |
| Oxalic Acid (6% w.t. (0,6 M), 50 V) | 37 | 100 | 10¹⁰ | 12,4 |
| Oxalic Acid (2,7% w.t. (0,3 M), 40 V) | 28 | 88 | 2 x 10¹⁰ | 9,1 |
| Al film thickness before anodization: 30 nm |
| Sulfuric Acid (6% v.v. (1 M), 20 V) | 16 | 45 | 8 x 10¹⁰ | 11,5 |
| Sulfuric Acid (2,7% v.v. (0,5 M), 25 V) | 12 | 50 | 6 x 10¹⁰ | 5,2 |
| Oxalic Acid (6% w.t. (0,6 M), 30 V) | 13 | 53 | 5 x 10¹⁰ | 5,4 |

If we compare these results with results in the literature, we obtain a general agreement for the case of 500 nm thick films [3-5]. More specifically, anodization in sulfuric acid results in smaller pore diameters with higher pore densities than anodization in oxalic acid. The obtained pore diameter and inter-pore distance agree also with results in the literature. On the contrary, in the case of ultra-thin alumina films from anodization of 30 nm thick Al films, the resulting film structure is similar in both electrolytes. In that case the pores were much narrower than in the case of thicker films, anodized under the same conditions. An example is illustrated in figure 4, where we show four plan-view bright field TEM images of four porous alumina films obtained by anodization of 4 pure Al films, 30 or 500 nm thick on Si, in 0,5 M sulfuric acid, anodization voltage 20 V (a, b), and in 0,3 M oxalic acid, anodization voltage 40 V (c and d). In (a) and (c) the thickness of the Al film before anodization was 500 nm, while in (b) and (d) it was 30 nm. The circle around each pore that we observe in images from thinner samples reflects a void of larger diameter below the pore; identified in cross sectional TEM images [12] (see also figure 3a).
Figure 4. Porous alumina films obtained by anodization in 0.5 M sulfuric acid under constant voltage of 20 V (a), (b) and in 0.3 M oxalic acid under constant voltage of 40 V (c), (d). In (a) and (c) the anodized Al film was 500 nm thick, while in (b) and (d) it was 30 nm thick.

We have to note here that by changing the anodization conditions, it is possible to find conditions for which the resulting films are identical for both thicker and thinner films. These conditions were as follows: sulfuric acid, 1M, under anodization voltage of 20V.

Nielsch et al. in [14] claim that in order to have a uniform self-ordering of porous alumina in hexagonal close packed arrays, the porosity should be about 10%. This has been verified in our experiments. By calculating the porosity for the cases of table I, we observe that for our thicker samples, where the pores are uniformly distributed in hexagonal close packed arrays, the porosity is about 10%, and the other parameters are very close to those found by Nielsch et al. in reference [14], for similar anodization conditions. This also applies for the first case of the ultra thin films. On the contrary, in the last two cases of table I, where the pores are not so well distributed in a hexagonal structure, the porosity value is about 5%.

3. Conclusions
The conditions for the fabrication of very thin porous anodic alumina films on a silicon substrate were investigated in this paper. Two different electrolytes were used and electrochemical conditions were found for the fabrication of alumina films with thickness as small as 50 nm, with uniform vertical pores distributed in hexagonal close packed arrays. Some appropriate anodization conditions were found, which resulted in the same film structure for both thicker and thinner films, namely anodization in sulfuric acid 1M, under constant voltage of 20 V.

4. References
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