

Confinement Effects in Nanoscale Anodic Alumina Structures on Silicon

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ABSTRACT

Anodic aluminum oxide (AAO) has long been considered a viable material for templated growth of nanomaterials for electronic, magnetic and optical applications due to the ability to form self-organized, high aspect-ratio nanochannels. More recently these porous materials have been incorporated with silicon to create a template for nanostructured materials on a semiconducting substrate. However, there has been no investigation into how pore growth is affected by confining the pre-anodized aluminum dimensions to the nanometer scale. We have used electron beam lithography to pattern 200 nm thick aluminum structures on Si with lateral features ranging from 100 nm to several microns in size. Structures consisting of 1 – 10 individual pores 10 – 15 nm in diameter are routinely fabricated. Confinement effects in the narrowest features assist in pore ordering in the porous structures without the use of pre-patterning or a two step anodization.

INTRODUCTION

Anodic aluminum oxide membranes and films were first discovered in the 1940's by Keller and Edwards.¹ Until the last decade the AAOs saw interest primarily as filtration devices. More recently the AAOs have seen an increased amount of interest due to the recent activity in nanoscience and technology. The membranes provide highly ordered nanoporous arrays as a means for relatively simple and inexpensive methods of templating, scaffolding and patterning a wide range of materials for potential uses in electronic, magnetic and optical applications.²⁻⁵

Porous alumina is formed via an electrochemical process. Under the proper conditions the pores order themselves into a close-packed formation. The ordering has been attributed as a reaction to the mechanical stress that exists upon the conversion of aluminum to aluminum oxide and the subsequent volume expansion.⁶ This highly ordered pore configuration is achieved on bulk Al through a lengthy two-step anodization producing membranes up to 200 μm thick with ordered domains up to several microns in lateral size. For the silicon integrated AAO films the aluminum thickness is limited due to the metal deposition process. This was problematic as the established method of achieving well-ordered porous films requires at least tens of microns of Al and therefore cannot be applied on Si. Recently significant progress has been made in finding alternate methods to creating ordered porous films. By pre-patterning the aluminum via several different methods including a mechanical imprinting process^{3,7}, focused ion beam milling⁸ and holographic patterning⁹ highly ordered porous films have been fabricated.

Previously during AAO fabrication the oxides have been prepared with bulk lateral dimensions. In an effort to create discrete, addressable regions of porous alumina and to investigate the effects of confinement that occur when the lateral dimensions of the structures are

on the order of the pore diameter we have confined the aluminum films in the lateral dimensions on the nano and microscale via two techniques. Since anodization is an electrochemical process both methods had to take into account the application of a potential across the aluminum regions. To apply this potential a highly doped silicon wafer was used to allow current to flow to the isolated structures and the aluminum itself was used in the case of a continuous aluminum network. We have investigated the fabrication of these confined AAO structures and the effects nanoscale confinement has on the pore distribution, spacing and ordering.

EXPERIMENTAL DETAILS

Fabrication of the aluminum structures was accomplished using e-beam lithography and a standard lift-off technique. First, 950,000 MW PMMA in anisole was spin-coated onto a silicon wafer. For the isolated structures on the highly doped wafer $\langle 110 \rangle$, 0.048-0.064 Ω cm *n*-type boron doped silicon wafers were used. In the case of continuous network on the lightly doped wafers $\langle 111 \rangle$, 1-10 Ω cm *n*-type wafers were used. The patterning was written with a LEO 1530 field emission scanning electron microscope and developed in a 1:3 MIBK:IPA solution for 1 minute. Development was terminated by an IPA rinse and drying with a flow of N₂. Aluminum films of 200 nm thickness were then deposited onto the patterned wafer using a CHA-600 e-beam evaporator. Finally an acetone bath was used to dissolve any undeveloped PMMA and lift-off the aluminum from the unpatterned regions.

Samples were ion-milled with 3 keV argon ions for 3 minutes to provide a more uniform surface for anodization. Anodization was then carried out with voltages between 20 – 25 V in the case of the isolated regions and 40 V for the extended aluminum networks. Anodization was performed in a 0.3 M oxalic acid solution with a platinum sheet acting as a cathode. A typical anodization was carried out for 100 seconds. In some cases ion-milling was also used after anodization to present a more planar surface for imaging. Samples were analyzed and imaged using a LEO 1530 scanning electron microscope after sputtering a thin gold coating.

DISCUSSION

As described previously, two methods of forming confined porous regions were utilized. Although both methods were successful, they resulted in different nanopore structures. The first

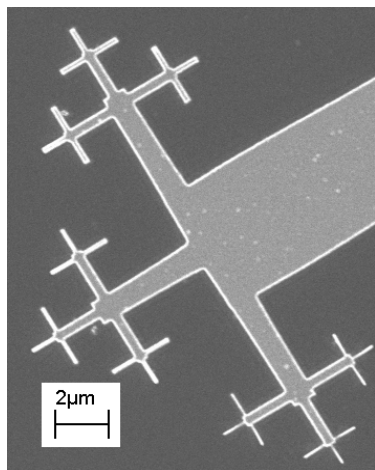


Figure 1. SEM micrograph of a portion of the as deposited aluminum network.

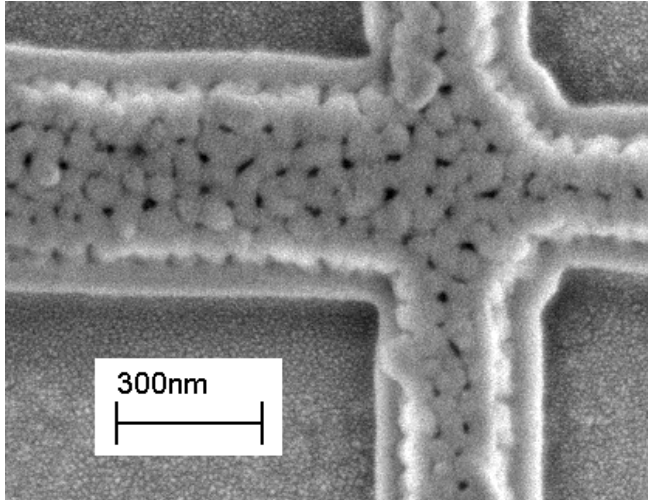


Figure 2. SEM micrograph of aluminum network anodized at 40 V. The angle of the sidewalls as well as the perimeter structure seen here are artifacts of the aluminum deposition process.

method entailed the use of lightly doped silicon substrate and a continuous aluminum network (Fig. 1) to supply current for the anodization process. The network was patterned around a central strip of Al with a width of 50 μm and a length of several millimeters. Smaller features sprouted off the central element that progressively decreased in size in a fractal manner down to the nanoscale as demonstrated in Fig. 1. Porous structures were fabricated at the nano (Fig. 2) and microscale using this method. Using the aluminum as the electrical contact allows a wide range of anodization conditions to be used. This allows for a great deal of control over the pore size and spacing. However, this technique requires an extensive amount of e-beam patterning.

The second method utilized heavily doped n-type silicon wafers with conductivity high enough to allow the supply of current to isolated aluminum islands (Fig. 3). The use of the heavily doped substrate allowed for more flexibility in the design of the aluminum regions when compared with the continuous network. Again porous structures at both the micro and nanoscale (Figs. 4 and 5) were formed. As shown in Figure 5, structures a few hundred nanometers in size were found to produce only a few pores.

Despite the success of this technique the use of the highly doped substrate required the reaction conditions to be altered. When a voltage is applied to the doped wafer it reacts with the

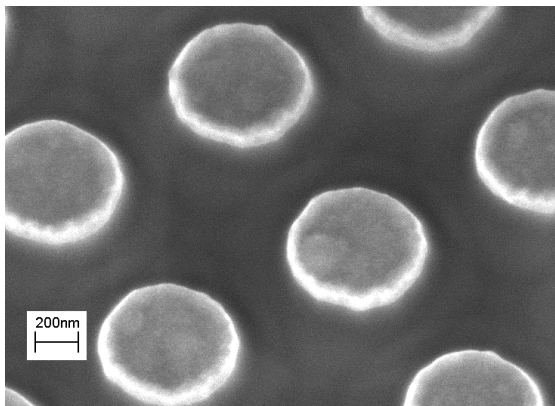


Figure 3. Image of unanodized aluminum structure array on highly doped substrate.

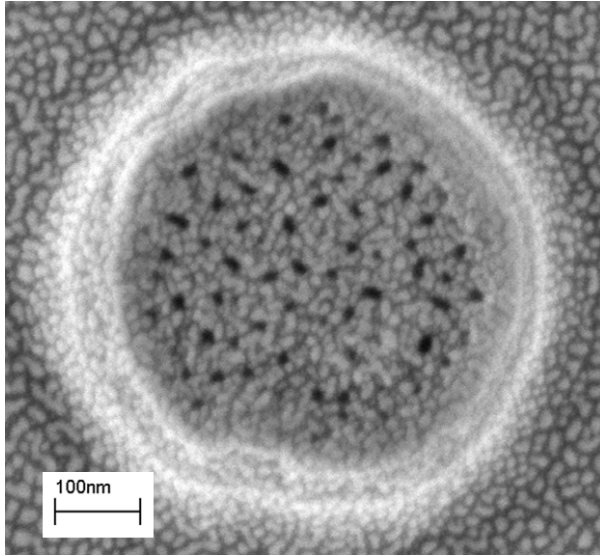


Figure 4. SEM micrograph of an isolated 100 nm thick aluminum structure with a diameter of 550 nm anodized at 25 V on a highly doped wafer. The granular surface is due to the gold sputtering of the structures for imaging.

oxalic acid. At voltages higher than 30 V the reaction completely poisons the anodization process. To avoid this problem anodization voltages were kept to 25 V or less. However, this voltage limit restricted the size of the pores formed. The range of pore diameters was further limited by the silicon serving as the electrical conduit, whereby the proportionality between voltage and pore diameter that is typically exhibited in the formation of AAOs was found not to apply.

Crouse *et al.*¹⁰ reported a ratio of 1.29 nm V^{-1} with bulk films grown on a 1-10 $\Omega \text{ cm}$ wafer. In this configuration the aluminum itself serves as the electrical contact. The isolated structures that used silicon as the electrical conduit demonstrated a proportionality of $0.45 - 0.55 \text{ nm V}^{-1}$, less than half that observed by Crouse. We attribute this decrease in pore size to the competing reaction of the doped wafer with the acid solution. Even at voltages below 30 V the oxidation of the Si proved to be sufficiently reactive to interfere with the pore formation. The

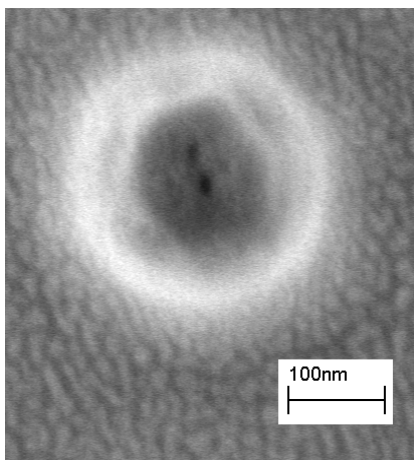


Figure 5. SEM micrograph of an AAO structure 270 nm diameter in diameter with two individual pores.

pore size reduction may also be in part due to the nonuniform contact between the Si and the aluminum islands. It should be noted that the native oxide of the silicon wafers was not removed in our experiments.

In unpatterned aluminum, anodization yields randomly distributed pores. As previously mentioned aluminum films pre-patterned with impressions have been used to fabricate highly ordered porous films. No pore initiation sites were patterned onto the aluminum structures prepared here. Without this pre-patterning pores tend to initiate in these materials at grain boundaries and defects. As expected, no high-degree of hexagonal ordering was observed in these structures. However, upon extreme confinement in one lateral dimension a pore ordering effect was observed. When one of the lateral dimensions was kept constant and the other was simultaneously reduced a shift from a random pore orientation to a relatively ordered array was observed (Fig. 6). This effect was observed to occur once the reduced dimension reached an approximate value of 150 nms. Note that this ordering of pores was achieved without the use of mechanical pre-patterning of the aluminum or a two-step anodization. This ordering was enhanced due to the lack of pore formation near the structure perimeters (Fig. 2). This edge-exclusion effect will be discussed in more detail elsewhere.¹¹

The pore initiation and development that occurs in the confined structures is similar to that observed in mechanically patterned porous thin-films. The patterned films pore ordering is induced by forcing the pores to initiate in a pre-set lattice. In the case of the confined regions fabricated here, the pores are not patterned into the aluminum rather the pores are forced into an arrangement simply by the lack of material to develop in. The degrees of freedom of pore growth are so severely limited that the pores can either develop in the thin region of alumina or not at all. In both cases the films are sufficiently thin that the pore development is not disturbed by the self-arrangement process that occurs in bulk porous alumina due to the rapid growth of the pores.

This ordering was observed only in the extended aluminum network. This is attributed to the fact that in order to achieve such ordering the pore size and structure size must be in the correct proportion. Due to the smaller size of the pores formed in the isolated structures the match between pore and structure size was not achieved using this technique.

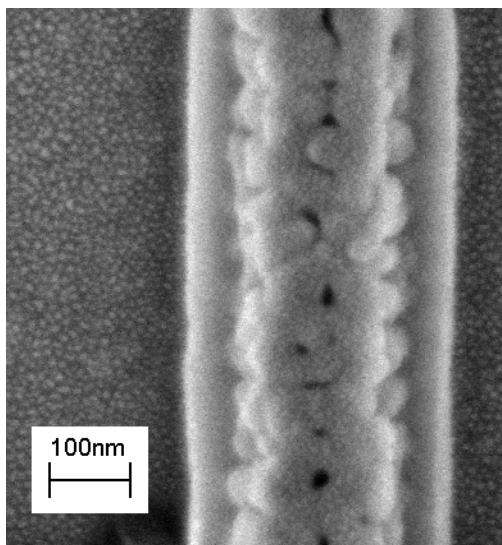


Figure 6. SEM micrograph showing one-dimensional ordering of the pores under extreme confinement in the extended aluminum network.

CONCLUSIONS

Porous aluminum oxide can be prepared in confined nanoscale regions. These structures can be fabricated with e-beam lithography using two methods. The first method involves patterning an extended aluminum network which allows a wide range of anodization conditions resulting in a high degree of control over pore size and spacing. The second technique involves patterning isolated aluminum islands and thus requires a highly doped substrate to act as an electrical contact between the voltage source and the isolated aluminum regions. This method allows for only under a small range of anodization conditions due to the reactivity of the wafer, sacrificing control over pore size but enhancing the range of shapes that can be fabricated. Use of wafers with an intermediate level of doping may provide a suitable resolution to the difficulties experienced with the two techniques.

A significant degree of nanopore ordering was observed due to extreme one-dimensional confinement in the case of the networked structure. These ordered structures demonstrate that pore ordering can be induced in AAOs without the use of a two-step anodization or mechanical pre-patterning of the aluminum. The confinement induced ordering combined with the ability to fabricate structures containing individual pores demonstrates that highly tailored AAO structures can be created.

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REFERENCES

1. J.D. Edwards, F. Keller, *Trans. Electrochem. Soc.*, **79**, 135 (1941).
2. J.C. Hulteen, C.R. Martin, *J. Mater. Chem.*, **7**, 1075 (1997).
3. I. Mikulskas, S. Juodkazis, R. Tomašiūnas, J.G. Dumas, *Adv. Mater.*, **13**, 1179 (2001).
4. S. Pan, L.J. Rothberg, *Nano Letters*, **3**, 811 (2003).
5. G.S. Huang, X.L. Wu, Y. Xie, X.F. Shao, S.H. Wang, *J. Appl. Phys.*, **94**, 2407 (2003).
6. O.Jessensky, F.Muller, U.Gösele, *Appl. Phys. Lett.*, **72**, 1173 (1998).
7. T. Yanagishita, M. Sasaki, K. Nishio, H. Masuda, *Adv. Mater.*, **16**, 429 (2004).
8. N.W. Liu, A. Datta, C.Y. Liu, Y.L. Wang, *Appl. Phys. Lett.*, **82**, 1281 (2003).
9. Z. Sun, H.K. Kim, *Appl. Phys. Lett.*, **81**, 3458 (2002).
10. D.Crouse, Y.H. Lo, A.E. Miller, M.Crouse, *Appl. Phys. Lett.*, **76**, 49 (2000).
11. P.J. Griffin, R.W. Carpick, D.S. Stone, in progress.