

Microstructured horizontal alumina pore arrays as growth templates for large area few and single nanowire devices

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We demonstrate the fabrication of horizontally aligned and well-defined nanopore structures by anodic oxidation of aluminum thin films and micro stripes on a Si substrate. We are able to control both, the pore diameters and interpore distances from 10 nm to 130 nm and from 30 nm to 275 nm, respectively. The anisotropy of the system induces some deviations in the pore configuration from the typical honeycomb structure. By decreasing the dimensions of the Al structures, the final pore

diameter and interpore distance remains constant, enabling the transition from multiple to a few nanowire porous structures. Finally, we successfully filled the nanopores by pulsed electroplating, as demonstrated both by Scanning Electron Microscopy and by current–voltage measurements. Having full control over the size, the density, the position and the orientation of the porous structure, our approach is promising for many exciting applications, including nanoelectronics and sensing.

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One-dimensional structures have attracted a great interest in the last two decades in broad areas of nanotechnology, such as electronics, sensing, and information technology. For future applications, one of the biggest challenges is their controlled organization on a substrate. An elegant approach is template growth, in which a preexisting structure defines the nanowires geometry. Porous anodic aluminum oxide (AAO) film has attracted much interest due to the high aspect ratio, high degree of ordering, high pore density, uniformity and low cost synthesis [1–3]. AAO templates are commonly obtained with the pores oriented vertically on a substrate [4, 5]. Unfortunately, this method offers some difficulties for their compatibility with the mainstream Si planar technology. However, a significant advance has been achieved in the last years towards the fabrication of horizontal AAO templates on a chip [6, 7].

In this letter, we present a substantial progress in a template based method, which can be used for the planar alignment and positioning of single nanowires on a chip, e.g. for the direct parallel fabrication of multiple transistors.

Our sample design and experimental setup are schematically illustrated in Fig. 1. The anodized structures con-

sist of Al thin stripe structures, encapsulated under a SiO₂ layer to ensure electrical isolation. The fabrication process is as follows: As a substrate, a thermally oxidized silicon wafer with a 1 μm thick SiO₂ layer was used. First, 1 μm Al thin film (99.99% purity) was thermally evaporated on the substrate. The wafer was then annealed at 480 °C for 3 h in a forming gas atmosphere and cut into 1 cm × 1.5 cm pieces. The Al thin film was patterned into macroscopic stripes or microscopic fingers by optical photolithography.

To define the structures, the Al was wet chemically etched with an ANPE solution. A 500 nm thick SiO₂ capping layer was deposited on top by plasma enhanced chemical vapor deposition (PECVD) at 350 °C. A macroscopic back contact for anodization was defined at the end of the Al stripe by etching the SiO₂ with a 10% HF solution. Finally, the piece was cleaved and immersed into the electrolyte. Two different sample structures were investigated: macroscopic stripes (Fig. 1a) and microscopic finger arrays (Fig. 1b), with different stripe widths. The anodization experimental setup is shown in Fig. 1c. A standard Teflon electrolytic cell is provided with a platinum mesh at

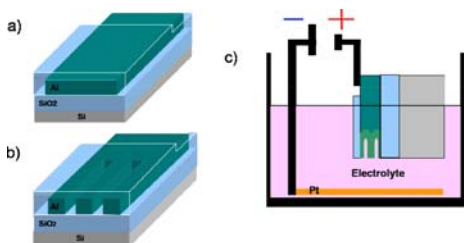


Figure 1 (online colour at: www.pss-rapid.com) Sample design and experimental setup. a) Al thin stripe structure and b) finger array structures for the fabrication of a) a horizontal porous alumina thin film membrane and b) isolated porous alumina membranes at the micro and nanoscale. c) Electrochemical cell for the anodization of the encapsulated Al structures shown in a) and b).

its bottom as the cathode. The bottom of the cell is cooled with a low temperature fluid circuit to ensure a constant anodization temperature of 0 °C. For the anodic oxidation process, three different solutions at different voltage ranges were used. Following the standard procedures, all samples have been processed through a two-step anodization process to ensure a higher degree of arrangement [4]. Three different solutions were used for different voltage ranges: sulfuric acid for voltages from 10 V to 20 V, oxalic acid from 20 V to 40 V, and phosphoric acid for voltages from 50 V to 130 V, in accordance with the conventional anodization conditions for planar porous AAOs [5, 8]. The morphology was investigated by scanning electron microscopy (SEM).

We have explored the full parameter space for the anodization conditions of the macroscopic Al stripes. Representative SEM images of AAOs obtained with each of the solutions are shown in Fig. 2a–c. The porous thin films obtained with sulfuric acid exhibit very small pores (down to 25 nm) and a hexagonal arrangement throughout the cross-section of the layer. The pore diameter and interpore distance of AAOs increased when oxalic acid was used, but the arrangement of pores is still honeycomb-like. The largest pores and interpore distances were obtained with phos-

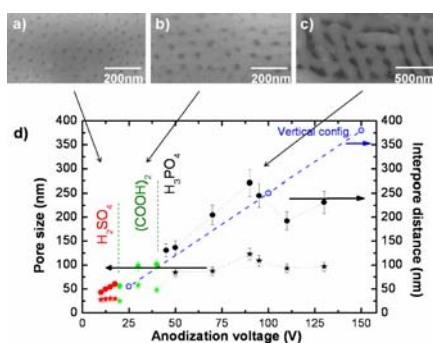


Figure 2 (online colour at: www.pss-rapid.com) Typical SEM images of samples obtained with the three types of solutions: a) 0.3 M H_2SO_4 (20 V), b) 0.3 M $H_2C_2O_4$ (40 V), c) 0.4 M H_3PO_4 (90 V). d) Pore size (*) and interpore distance (●) of the horizontal porous alumina membranes as a function of the anodization conditions. The results are compared with the conventional vertical configuration results (blue dashed line).

phoric acid. In this case a quadratic arrangement of pores was obtained. This occurs only when the interpore distance is about one fourth of the film thickness, namely ~ 225 nm.

The reason of the different arrangement in the latter case can be explained by the existence of an anisotropic stress provided by the encapsulating SiO_2 layer. We suggest that in this case, the quadratic arrangement is the more energetically preferable one to release the stress, which can be understood as follows. In the anodization of an “infinite” planar thin film, the stress due to the increase of volume during anodization is released equally in all directions, giving rise to a hexagonal pore arrangement. In the stripe case, the stress can be released differently in the two directions (perpendicular and parallel to the surface), which results into a quadratic pore arrangement. Similar tendencies have been observed in the self-assembly of spherical block polymer arrays [9]. Results on the pore diameter and the interpore distance as a function of the applied voltage are plotted in Fig. 2d. The size of both features increases with the applied voltage. For comparison, we have added the interpore distance obtained in the past for vertical AAO [5, 8]. The interpore distance increases linearly with the applied voltages up to a value of $>225 \pm 25$ nm, where it saturates. This saturation occurs approximately at one fourth of the total film thickness. At the same time, the geometrical arrangement of the pores changes from honeycomb to quadratic which indicates the transition of the anodization process from infinite-like to finite dimensions. The diameter of the pores exhibits a different behavior, as it only tends to increase about 5% with the voltage and is more directly related to the solution used for the anodization. With sulfuric acid a diameter of $25 \text{ nm} \pm 5 \text{ nm}$ was obtained, while for oxalic and phosphoric acid the diameters were $50 \text{ nm} \pm 10 \text{ nm}$ and $90 \text{ nm} \pm 10 \text{ nm}$, respectively. The independent control of the pore diameter and interpore distance provides a design freedom that can be of great advantage in certain.

The fabrication of finger arrays constitutes a step forward towards the fabrication of nanoscopic isolated devices. By changing the width of the fingers the number of pores per device can be easily controlled. Here we demonstrate that the same principles can be applied when reducing

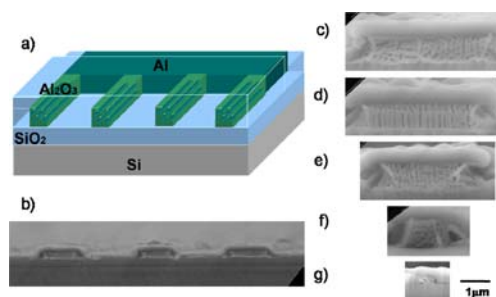


Figure 3 (online colour at: www.pss-rapid.com) a) General sketch of finger design, and SEM images: b) finger array, and individual fingers with widths c) 5 μm , d) 4 μm , e) 3 μm , f) 1 μm and g) 0.75 μm . All samples were anodized at the same anodization conditions (0.4 M H_3PO_4 (70 V)).

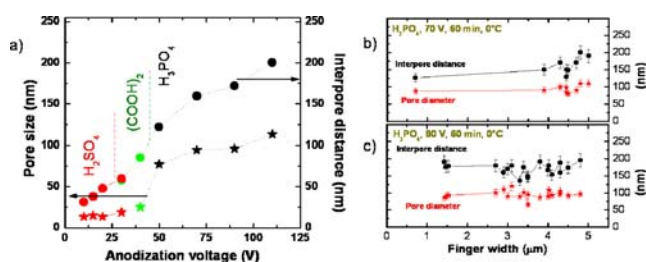


Figure 4 (online colour at: www.pss-rapid.com) Pore size and interpore distance a) versus anodization voltage of fingers and b), c) as a function of the finger width for finger structure. Conditions used: b) 0.4 M H₃PO₄ (70 V), c) 0.4 M H₃PO₄ (90 V).

the size of the stripes. Additionally, when brought to the extreme, single nanopore per finger can in principle be obtained.

We have explored the parameters of anodic oxidation in the confined geometry of finger stripes. As observed in the case of macroscopic stripes, the interpore distance increases with the applied voltage and the diameter is mainly dependent on the solution used. We observed however a smaller interpore distance and diameter, as manifested in Fig. 4a. Furthermore, we observed a hexagonal arrangement in smaller pores and quadratic arrangement for the largest interpore distances. The arrangement of the finger structures is shown in Fig. 3. We investigated finger samples, where the width of the fingers was varied from 10 μm down to 750 nm. It is of prime interest to show the effect on the final pore structure morphology when reducing the Al stripe width for obtaining single pore structures. The anodization conditions were applied on stripes with widths down to 750 nm. The morphology did not exhibit any significant finger width dependence. This is clearly depicted in Fig. 4b and c, where the size and interpore distance of fingers with widths between 5 μm and 0.75 μm were shown for anodization conditions: 0.4 M phosphoric acid at 0 °C and 70 V and 90 V. The pore diameter and the interpore distance remains constant at 90 nm ± 10 nm and 180 nm ± 10 nm, respectively.

The pores were filled with nickel using pulsed electro-deposition [10]. In order to ensure the ionic transport to the bottom of the pores, special attention was made to remove the barrier layer (see Supporting Information, 1, online at: www.pss-rapid.com). The pore filling with the consequent wire growth occurs through the ionic current along the pore direction up to the pore openings. After 3 h the membrane was filled as indicated by resulting deposition at the end of the pores. An identical filling time was observed for the other membranes, indicating a growth rate independent of pore size. An SEM image of a membrane exposed to the 3 h filling procedure is shown in Fig. 5a and b. About one fourth of the pores were filled. One explanation for the existence of unfilled pores is the inhomogeneity in barrier layer thinning process, as the current flows in areas with higher conductivity (thinner barrier layer). To further demonstrate the filling we performed electric transport measurements. As schematized in the inset of Fig. 5c, an Al

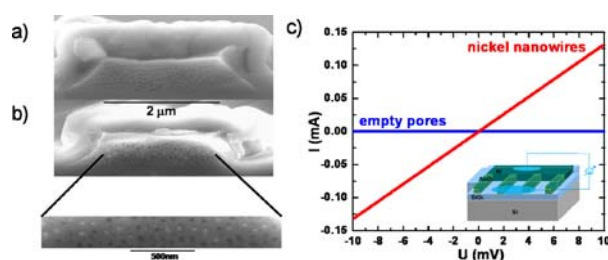


Figure 5 (online colour at: www.pss-rapid.com) Representative SEM micrographs of a finger structured AAO template: a) before and b) after electro-deposition with Ni. c) Current–voltage characteristics of a finger structured AAO with empty (blue line) and Ni-filled nanopores (red line).

electrical contact was thermally evaporated on the membrane side and the current was measured between the two ends. Control experiments on unfilled PAA arrays were also done. As shown in Fig. 5c, when a voltage sweep is applied to the sample within the range of –10 mV to +10 mV, the current is below the resolution limit. When the pores are filled with Ni, we observe a perfect ohmic behavior with a resistance of 75.7 Ω, which agrees well with the filling of one fourth of the total number of pores (see Supporting Information, 2, online at www.pss-rapid.com).

In summary, we have fabricated horizontally aligned and well-defined nanopores by two-step anodic oxidation of aluminum thin films and microscopic fingers on a Si substrate. We were able to control both, the pore diameters and interpore distances from 10 nm to 130 nm and from 30 nm to 275 nm, respectively. Due to the anisotropy of the system, the global pore arrangement changes from honeycomb structure to a quadratic. By decreasing the finger lateral width, the pore diameter and interpore distance remain constant, enabling the transition from multiple to single and few nanowire structures. We further demonstrate that metal nanowires can be grown inside the pores via pulsed electro-deposition.

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References

- [1] T. P. Hoar and N. F. Mott, *J. Phys. Chem. Solids* **9**, 97 (1959).
- [2] G. E. Thomson et al., *Nature* **272**, 433 (1978).
- [3] G. E. Thompson and G. C. Wood, *Nature* **290**, 230 (1981).
- [4] H. Masuda and F. Fukuta, *Science* **268**, 1466 (1995).
- [5] A. P. Li et al., *J. Appl. Phys.* **84**, 6023 (1998).
- [6] H. Masuda et al., *Appl. Phys. Lett.* **63**, 3155 (1993).
- [7] C. S. Cojocararu et al., *Nano Lett.* **5**, 675 (2005).
- [8] K. Nielsch et al., *Nano Lett.* **2**, 677 (2002).
- [9] V. P. Chuang et al., *Nano Lett.* **6**, 2332 (2006).
- [10] K. Nielsch et al., *Adv. Mater.* **12**, 582 (2000).