Optimization of anodized aluminum oxide pore morphology for GaAs nanowire growth

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ABSTRACT

Anodic Aluminum Oxide (AAO) films were produced by anodization of sputtered aluminum thin films on Silicon substrates. The effects of anodization voltage and aqueous oxalic acid solution on the pore diameter and interpore distance were studied. Parameters were sequentially varied to optimize the pore uniformity. Pore morphology was most uniform at 40V anodization voltage and 0.3M solution concentration. Average pore diameter and interpore distance for these parameters are 26.14nm ± 13% and 74.62 ± 8%, respectively. Pore diameter uniformity was further improved by etching with phosphoric acid solution. The AAO films were also successfully used to pattern gold nanoparticle catalysts for the synthesis of semiconductor nanowires.

Keywords: Anodic films, Electrolysis, Nanoparticles

INTRODUCTION

Anodic aluminum oxide (AAO) is one of the widely used templates in patterning nanoparticles. This is due to its relative ease of fabrication, mechanical strength, thermal stability, structural uniformity and tunability of the pore morphology (Kim, Kim & Cho 2006; Naitabdi, Ono, & Cuenya 2006; Masuda & Fukuda, 1995; Masuda, Hasegwa & Ono, 1997). These properties prove useful, for example, in the synthesis of nanoparticle catalytic synthesis nanowires. In this case, the nanowire properties are influenced by the nanoparticle dimensions which, in turn, are patterned by the AAO template (Gudiksen, Wang & Lieber, 2001; Gudiksen & Lieber, 2000).

AAO is a naturally-occurring, self-ordered porous structure. The geometry of the anodic porous alumina may be described as a honeycomb structure of columnar pores. These pores feature a high depth-to-diameter ratio as shown in Figure 1. The pore dimensions can be tuned via the anodization parameters (Masuda & Fukuda 1995; Masuda, Hasegwa & Ono, 1997). Wet etching can also be used to alter the pore dimensions and improve uniformity(Chen & Zhang, 2005; Masuda et al. 1997).

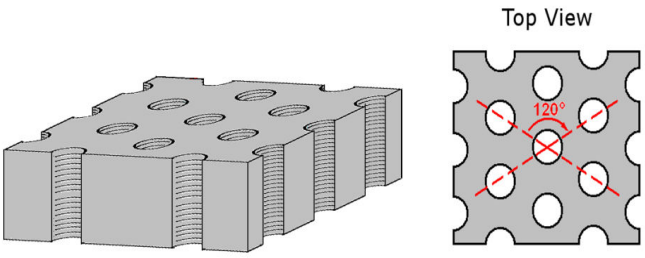


Figure 1. Schematic of an idealized honeycomb AAO structure.

In this work, AAO thin films were synthesized from Aluminum (Al) thin films on Silicon (Si) substrates. Anodization parameters were optimized to achieve the pore diameter and interpore distance uniformity. Effect of pore etching on the pore dimensions was also explored. In addition, the resulting AAO films were used to pattern gold (Au) nanoparticles which were subsequently used to synthesize III-V semiconductor nanowires.

METHODOLOGY

Pre-cleaned Si (111) substrates were deposited with Al thin films (~300nm) via RF magnetron sputtering. Anodization followed in an oxalic acid solution. Anodization parameters were based on the work of Masuda and Yamada (1997). The anodization voltage, solution concentration, and solution temperature were varied sequentially to optimize the AAO pore uniformity. Initially, the anodization voltage was varied (30V, 40V and 50V) while keeping the oxalic acid concentration constant at 0.3M. The resulting optimal anodization voltage was then carried over in the optimization of the other parameters. The oxalic acid concentrations used were 0.2M, 0.3M, and 0.4M and the solution temperatures used were 5°C, 15°C, and 25°C. Pore widening was subsequently done on the AAO thin films using 5% phosphoric acid solution at room temperature.

An anodization parameter was said to be optimized when the pore diameter and inter-pore distance standard deviations were minimized. Pore dimensions were measured using a Phillips Field Emission Scanning Electron Microscope (FE-SEM). Pore diameter was determined by measuring 50 randomly chosen pores while inter-pore spacing was evaluated by measuring 50 pairs of randomly selected pores.

In addition, the resulting AAO thin films were used to pattern Au nanoparticles which were used to grow III-V nanowires. Gold of 90Å film thickness was deposited on the AAO thin films via e-beam evaporation. The AAO thin film was then removed using a phosphoric and chromic acid solution leaving behind the Au nanoparticles. The resulting Au nanoparticles were then used to synthesize III-V nanowires via molecular beam epitaxy (MBE). Details of the Au nanoparticle and nanowire synthesis were reported elsewhere (Loberternos et al., 2008; Bailon-Somintac et al, 2010).

RESULTS AND DISCUSSIONS

A FE-SEM micrograph of the AAO film on Si is shown in Figure 2. Variation of the pore dimensions with the anodization parameters is shown in Figures 3-5. The y-error bars represent the standard deviation.

The variation of the pore diameter and interpore distance with anodization voltage are shown in Figure 3. The oxalic acid concentration is kept at 0.3M. The average pore diameter linearly increased with anodization voltage. This confirms that the pore diameter can be controlled by the anodization voltage. Similarly, the interpore spacing increased with the anodization voltage. Note that the pore diameter extrapolates to zero since anodization cannot occur when there is no anodization voltage. No significant difference was seen in the pore diameter uniformity for varying anodization voltages. However, it can be seen that the interpore distance uniformity was best for an anodization voltage of 40V. Pore diameter and interpore distance for this setting were 26.14nm ± 13% and 74.62nm ± 8%, respectively.

The variation of the pore diameter and interpore distance with oxalic acid concentration are shown in Figure 4. The optimized anodization voltage of 40V was used. A strong linear relationship can be found between the pore

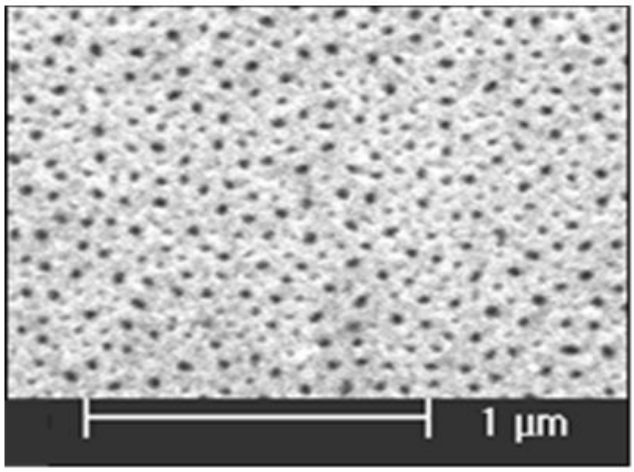


Figure 2. FE-SEM micrograph of anodized aluminum oxide (AAO) on silicon (Si) substrate.

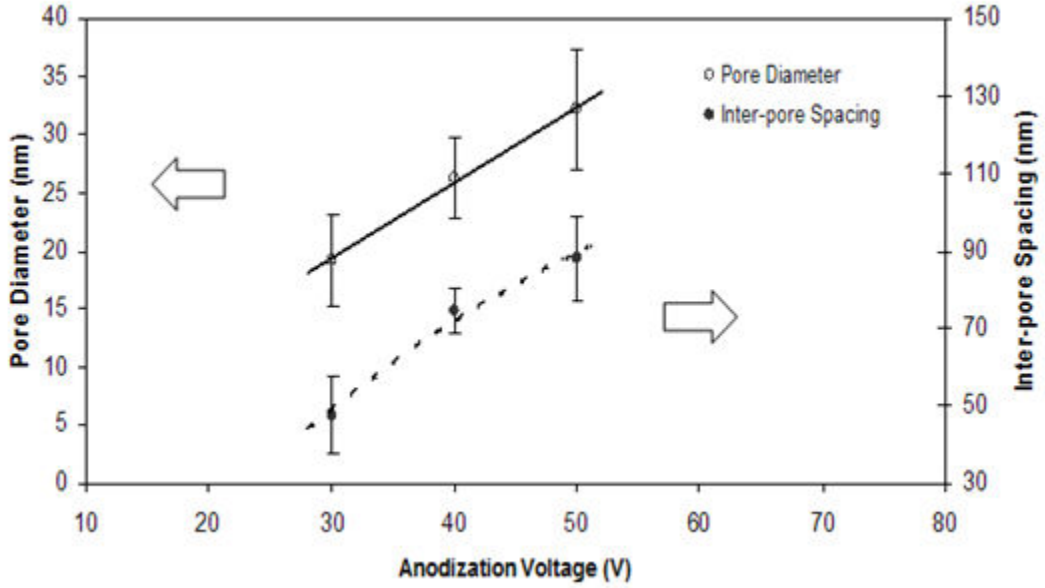


Figure 3. Variation of the AAO pore dimensions with the anodization voltage. The error bars represent the standard deviation.

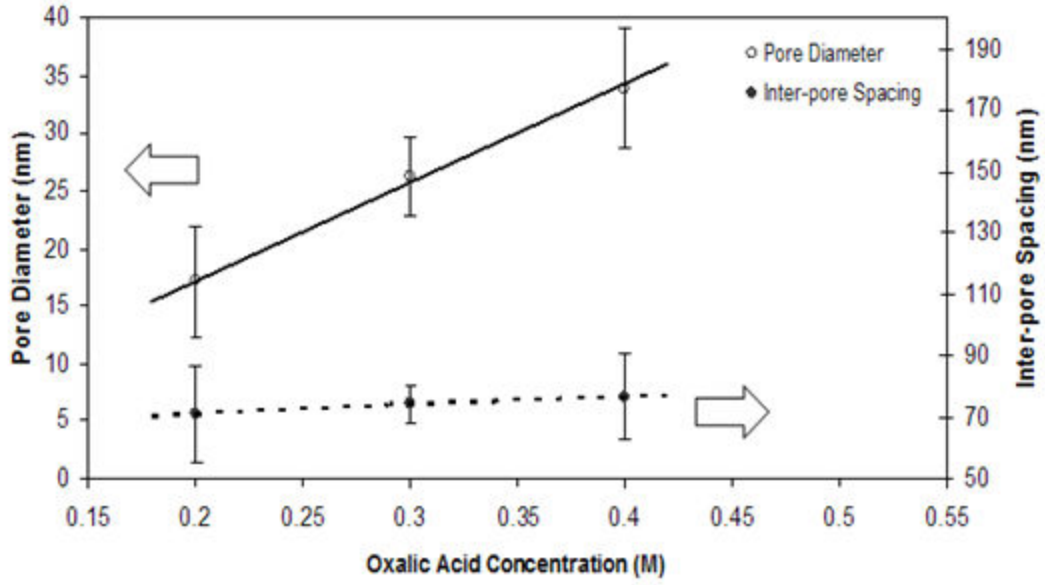


Figure 4. Variation of the AAO pore dimensions with the oxalic acid concentration. The error bars represent the standard deviation.

diameter and solution concentration. Note that the pore diameter can be extrapolated to zero since the anodization voltage is relatively low. The pore diameter and interpore distance was most uniform for a solution concentration of 0.3M.

The variation of the pore diameter and interpore distance with solution temperature are shown in Figure 5. The optimized anodization voltage (40V) and solution concentration (0.3M) were used. It was observed that the pore diameter and interpore distance were independent of the solution temperature. However, the interpore distance standard deviation was minimum at 5% for a solution temperature of 5°C.

Pore morphology was most uniform for an anodization voltage of 40V, oxalic acid solution concentration of 0.3M, and solution temperature of 5°C. The resulting pore diameter and interpore distance for these parameters were 26nm and 75nm, respectively. Pore diameter can be further increased by wet etching with 5% by volume phosphoric acid solution. Figure 6 shows the pore diameter variation with etching time. The pore diameter has a linear relation with the etching time; this allows for further control of the pore diameter. Furthermore, it can be observed that the pore diameters become more uniform with etching time. This is manifested in the decreasing trend of the pore diameter standard deviation with increasing etching time.

In addition, the resulting AAO pores were used to pattern Au nanoparticles which were then used in the catalytic synthesis of GaAs-based nanowires. Figure 7 shows the deposition of the Au nanoparticles and the resulting nanowires. Details of the nanoparticle and nanowire growth were reported elsewhere (Loberternos et al., 2008; Bailon-Somintac et al. 2010).

SUMMARY

Anodic aluminum oxide (AAO) was synthesized from aluminum thin films on silicon substrate via anodization with oxalic acid. Pore diameter and inter-pore spacing of AAO were found to be strongly controlled by the anodization voltage and concentration of the oxalic acid solution. Optimum parameters for uniformity of pore morphology were also determined. Etching using phosphoric acid further improved the pore uniformity. Furthermore, the obtained AAO-templates were used

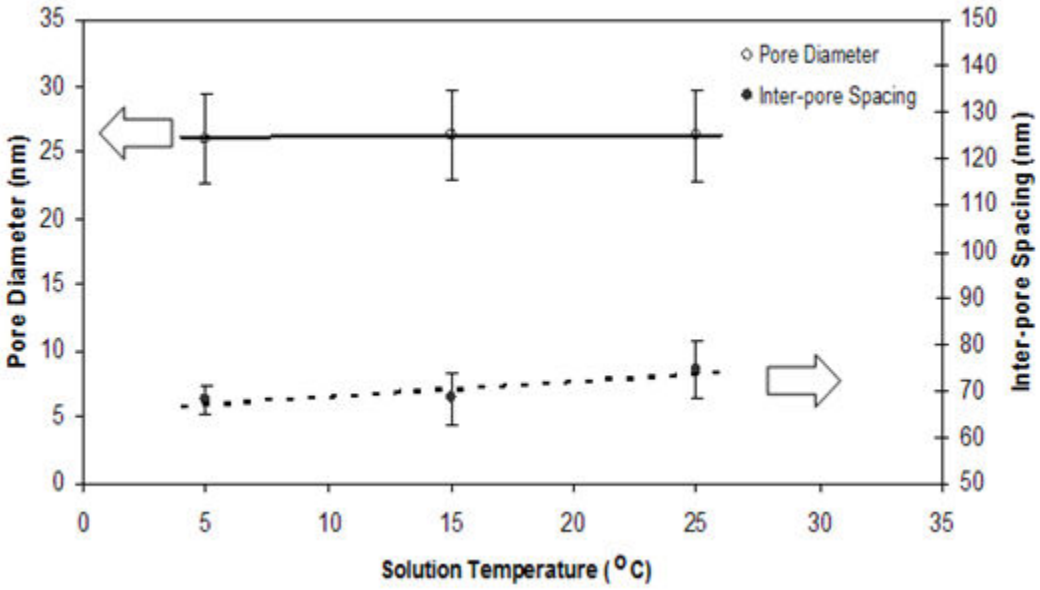
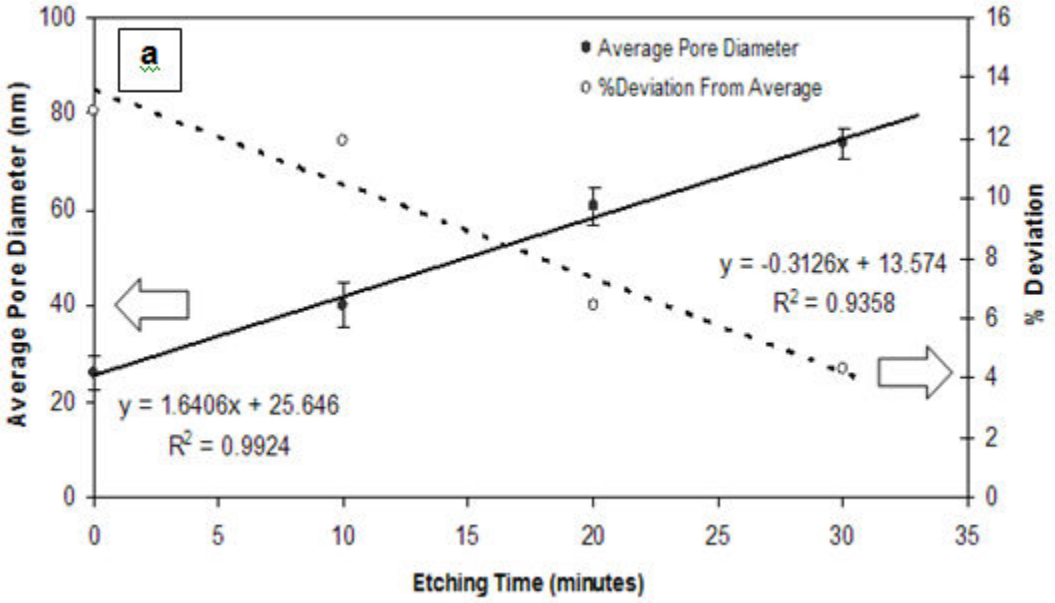


Figure 5. Variation of the AAO pore dimensions with the solution temperature. The error bars represent the standard deviation.



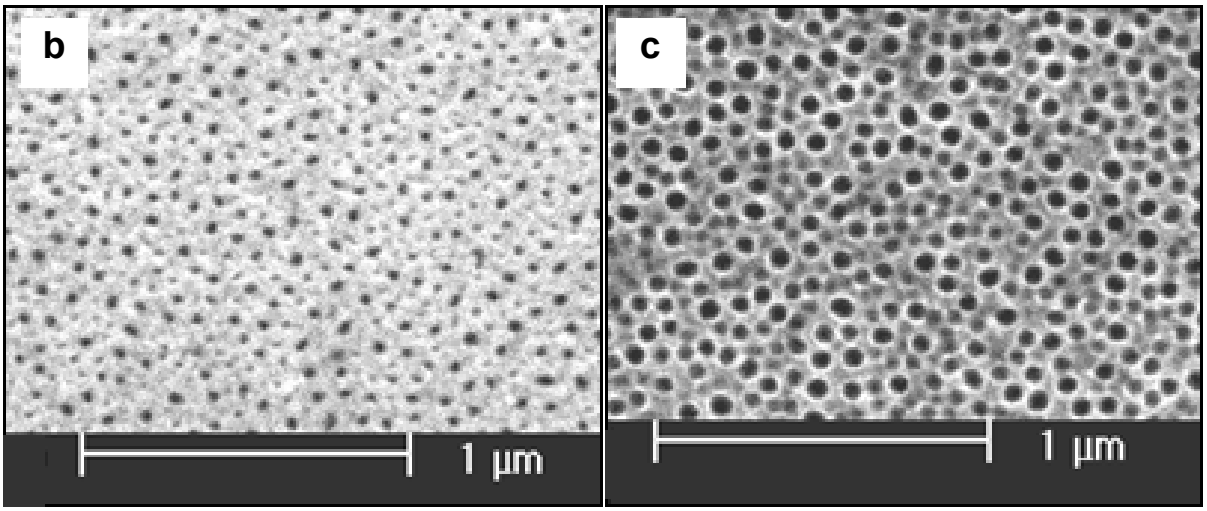


Figure 6. (a) Variation of the AAO pore diameter with the etching time. The error bars represent the standard deviation. FE-SEM micrographs of (b) as anodized sample and (c) after 20 min etching.

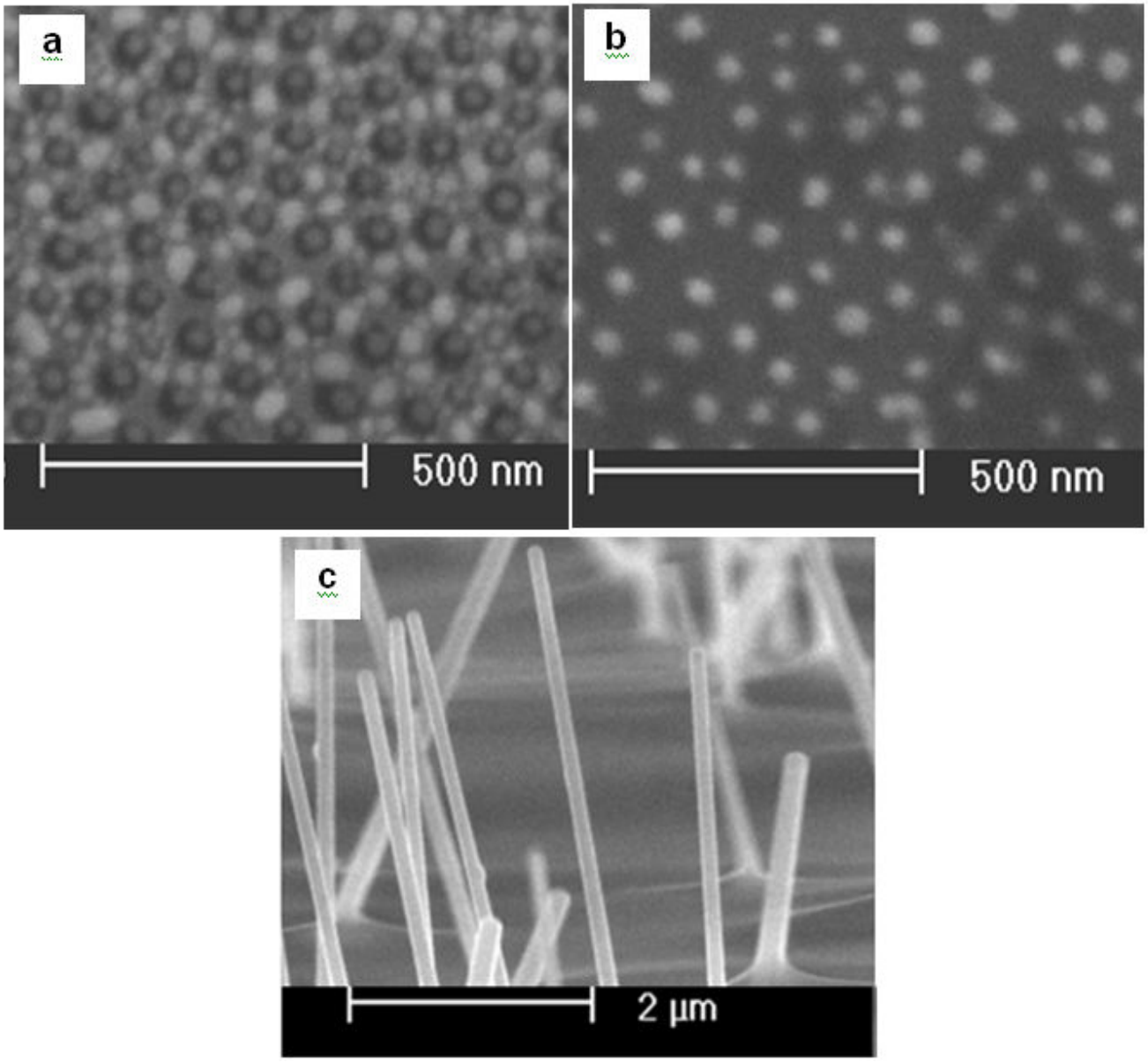


Figure 7. FE-SEM micrographs of the resulting AAO films for III-V nanowire catalytic growth. (a) Au deposited on Si substrate with AAO. (b) Au nanoparticles after removal (etching) of AAO. (c) III-V nanowires grown via MBE using the Au nanoparticle catalyst.

as a template for Au nanoparticles and III-V nanowire synthesis.

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