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Fabrication and characterization of aluminum oxide thin film micropatterns on the glass substrate

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ABSTRACT

This paper reports a standard lithography-based fabrication process of arrayed anodic aluminum oxide (AAO) thin film micropatterns on the glass substrate and the characterization of their optical properties. The fabrication process is compatible with the MEMS and microfluidics fabrication processes, and it offers great flexibility for fabricating a variety of shapes of AAO micropatterns as small as 5 μm. Experiments find that the optical properties of the as-fabricated AAO micropatterns remain unaffected by the chemicals used in the fabrication process. Specifically, the significant fluorescence enhancement capability and the unique optical interference characteristics of the AAO micropatterns remain unchanged. Due to the flexibility and compatibility of the fabrication process, the AAO micropatterns can be readily integrated on a single chip to form arrayed label-free biosensing technical platform or arrayed fluorescence-based technical platform for a variety of applications.

1. Introduction

Anodic aluminum oxide (AAO) probably is one of the most widely used nanostructures in the nanotechnology field. Specifically, AAO fabricated by an anodization process has been utilized for a great deal of applications in many different fields such as nanoscience and bionanotechnology [1–3]. For instance, the AAO has been extensively used as a template for nanofabrication. It has been used as a shadow mask to deposit metallic nanoscale masks for fabricating nanopillars. It has also been used as a template for fabricating a variety of nanotubes or hybrid nanomaterials by electroplating different materials into its nanopores. In addition, a category of label-free biosensor based on the AAO nanostructures has been developed for monitoring biomolecular binding and cancer biomarker detection [4–8], offering a promising technical platform with a great potential for high throughput applications. Recently, it has been found that the AAO substrate can also enhance fluorescence signals significantly over conventional glass substrates [9–12]. Different from the metal-enhanced fluorescence [13], the AAO substrate-based fluorescence enhancement does not require the coating of a thin layer of metal nanostructures such as the Au, Ag or other metals. The fabrication process of the AAO substrate is simple and cost-effective.

In order to be integrated with microdevices or microfluidic devices for both label-free biodetection and fluorescence-based biosensing, the micropatterned AAO is needed. To this end, one fabrication process has been developed recently [14]. The micropatterned AAO has been successfully fabricated on indium tin oxide (ITO) glass substrate by simply combining a lift-off process and an anodization (i.e., one-step or a two-step) process, in which the ITO layer is used to facilitate the current flow in the Al thin film during the anodization process [14]. However, this fabrication process has the following limitations: (1) Al microlines are required to connect the Al micropatterns to ensure that the current can flow to each micropattern during the anodization process. If the Al microlines have been anodized before the Al micropatterns are anodized, no current can flow through the Al micropatterns any more. As a result, the anodization process in Al micropatterns stops, and only part of them can be anodized. It has been reported that the anodization speed is related to the current, the selection of the anodization current is thus critical. (2) Since each micropattern has to be connected by Al microlines for anodization, the choices of shapes of the micropatterned AAO are limited. Otherwise, the micropatterns cannot be properly anodized. This limitation reduces the flexibility tremendously for designing different shapes of AAO micropatterns for some specific applications, and it could be a problem to integrate them into microdevices, including microfluidic devices. (3) Due to the reason discussed in (1), the feature size of the micropatterns is significantly limited. Experiments found that the minimum size of the AAO micropatterns, which can be fabricated with good yield using the current fabrication technique, is ~15 μm [14]. If smaller AAO micropatterns are needed, an alternative fabrication process becomes necessary. In order to address

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these aforementioned issues, herein we report a newly developed process for fabricating micropatterned AAO with a greater flexibility. And this process is compatible with the standard fabrication process for MEMS and microfluidics.

Typical determination technique of the AAO formation is based on the current change during the anodization process [15]. It also has been reported that the AAO has blue emission under UV light irradiance [16,17]. In addition, the intensity of the blue emission increases with the increased anodization time, due to the increased amounts of AAO formation and the increased density of the formed oxygen vacancies in AAO. The optical characterization (blue emission) offers an alternative approach for a rapid and nondestructive technique to determine if the Al has been anodized to be AAO or the degree of the anodization of Al has been achieved. This technique is especially useful for characterizing the AAO micropatterns. Finally, the optical properties, including the fluorescence enhancement capability and the unique optical interference characteristics, of the AAO micropatterns are evaluated, confirming that their optical properties remain unaffected by using the newly developed fabrication process.

2. Materials and methods

2.1. Materials and chemicals

ITO glass substrates are purchased from Nanocs, Inc. The sheet resistance of the ITO on the glass is 100 Ω/sq. The photoresist AZ 1512 and AZ developer are purchased from AZ Electronic Materials plc. The following fluorescent dyes are purchased and used in the experiments, including Rhodamine 6G (R6G) (Lightning Powder, Inc.), fluorescein sodium salt (FSS) (Sigma, Inc.), fluorescein isothiocyanate (FITC) (Sigma, Inc.) and fluorescent brightening agents (FBA) (Sigma, Inc.).

2.2. Fabrication process

The detailed new fabrication process is illustrated in Fig. 1a. The ITO glass substrate is washed thoroughly with four steps: it is washed by DI water, followed by Acetone, IPA, and DI water in sequence. After a 5-minute baking of the cleaned ITO glass, about 2 μm thick aluminum layer is deposited by E-beam evaporation as shown in Fig. 1b. The quality of the deposited Al is critical for successful anodization. One essential requirement is that the Al should be totally oxide-free, which means during E-beam evaporation, any oxidation of Al has to be avoided, otherwise the as-deposited Al cannot be anodized as found in our experiments. The other important requirement is the surface smoothness of the deposited Al. Measurements find its typical roughness is in the range of 6–12 nm [9–11], which is smooth enough for carrying out anodization, and further surface polishing is not required. This is a significant advantage compared to carrying out the anodization on the commercial Al foil sheet, which usually requires several steps to polish the surface of the Al sheet to ensure the surface is smooth enough [15].

Then we carry out anodization process (either one-step or two-step) in acid solution (0.3 M oxalic acid) with 45 V DC voltage at

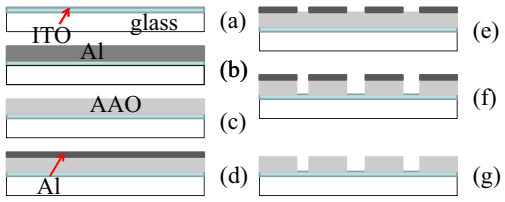

Fig. 1. Sketch of the fabrication process flow for AAO micropatterns.

2 °C to form AAO on the ITO glass substrate as shown in Fig. 1c. In this step, a layer of AAO is formed on the whole substrate. Specifically, for the one-step anodization process to form AAO [14], we only carry out one-step anodization on several samples for 25, 35, and 45 min, respectively. In contrast, for the two-step anodization process to form AAO [15], it takes 10 min for step-one anodization in 0.3 M oxalic acid, then the samples are etched by a mixture of phosphoric acid (0.4 M) and chromic acid (0.2 M) at 65 °C for 30 min, followed by a 40-minute step-two anodization in 0.3 M oxalic acid with the same experimental condition as the step-one anodization. The wafer is then rinsed by DI water rigorously. Thereafter, a 150 nm thick aluminum layer is deposited on the AAO surface by thermal evaporation as shown in Fig. 1d. Photolithography is then performed on the Al-coated AAO substrate. Specifically, a 1 μm photoresist (AZ 1512) layer is spin-coated at 4000 rpm on the substrate. Then the coated substrate is soft baked for 50 s at 95 °C. The micropatterns are then transferred and generated in the photoresist using the photomask through a 416 nm light exposure with a dose of ~70 mJ/cm^2, followed by a post-exposure bake for 50 s at 105 °C. The exposed photoresist is developed and removed by immersing in the AZ developer for 25 s. The patterned AZ resist serves as the mask to protect the Al underneath. The patterns are then transferred to the Al layer by etching the unprotected Al area in an etching solution {(H_3PO_4:CH_3-COOH:HNO_3:H_2O) 80:5:5:10 by weight%} for 35 s as shown in Fig. 1e. During this step, care should be taken to avoid any over-etching of the Al since the patterned Al layer serves as the mask for etching the AAO. Then the substrate is immersed in a mixture of phosphoric acid (0.4 M) and chromic acid (0.2 M) at 20 °C for 100 min to etch away the unprotected AAO and transfer the patterns into the AAO layer as shown in Fig. 1f. Thereafter, the remaining photoresist is washed away by dipping the substrate in acetone, followed by removing the Al layer by the Al etching solution. As a result, the AAO micropatterns on the substrate are obtained as shown in Fig. 1g. Again, in order to obtain the AAO micropatterns with high fidelity, the steps for etching Al and AAO are critical, and the etching time should be optimized. Otherwise, the resulting AAO micropatterns might be over-etched or under-etched. In addition, Al is chosen as the mask for the AAO layer instead of the photoresist as reported before since the thickness of AAO is ~2.5 μm [18–21]. It has been found that in most cases the photoresist cannot serve as a robust mask due to the long etching time (100 min) of the AAO layer. As a result, the micropatterns cannot be properly transferred directly from the photoresist to the AAO layer.

2.3. UV-characterization and data analysis

The UV characterization is achieved by an Olympus IX51 inverted microscope. The UV source is obtained from a mercury lamp by an optical filter: 330––385 nm. The UV light perpendicularly illuminates the sample, and the scattering light from the sample is collected by an Olympus DP71 Camera. To quantify the UV emission from different samples, the Imaging Processing toolbox in MatLab [9–11] is used. A MatLab program has been written to read and analyze the optical images. The program first converts the color image into a gray-scale image. Then, the intensity along a horizontal line is plotted according to the corresponding cutline drawn on the color image.

2.4. Fluorescence experiment

Rhodamine 6G (R6G), fluorescein sodium salt (FSS), fluorescein isothiocyanate (FITC), and fluorescent brightening agents (FBA) are used for the technical demonstrations. Solutions of these fluorescent dyes are uniformly coated on the micropatterned AAO and