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Nanoscale aluminum concaves for light-trapping in organic thin-films

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ABSTRACT

Anodic aluminum oxide (AAO) templates, fabricated from oxalic acid and phosphoric acid, lead to non-periodic nanoscale concave structures in their underlying aluminum layer, which are investigated for their field-enhancement properties by applying a thin-film polymer coating based laser ablation technique. Local ablation spots, corresponding to field enhancement on the ridge edges of the aluminum concave nanostructures, are observed in surface-covering polymer films, and confirmed with FDTD studies. The field enhancement leads to improved light absorption in the applied polymer layers, which may be used as an efficient method for enhancing the power conversion efficiency of organic solar cells.

1. Introduction

Light-trapping has been shown to have a positive effect on the performance of several devices such as sensors [1,2], where device sensitivity improvements due to enhanced absorption at a specific wavelength range have been demonstrated, and solar cells [3–5], where production of additional charge carriers arises due to enhanced light absorption in the active layers. Many mechanisms that have been introduced for light enhancement in inorganic thin films, however, are not applicable to organic films, due to the typical active layer thickness limitation of ~100 nm (e.g., in solar cells or light-emitting devices) [6–8]. Field enhancement in organic films by the use of plasmonic nanostructures has attracted much focus, as nanoparticles [9], nanomeshes [10], nanowires [11] etc. can be used to enhance light absorption in the organic films. The aforementioned enhancement methods, however, come at the price of expensive materials and usually slow and large-scale-incompatible fabrication processes.

Anodization of aluminum for the fabrication of anodic aluminum oxide (AAO) templates is a well-known and established technique [12–16] that can be used for fabrication of nanostructures such as nanowires [17,18], nanoparticles [18,19], nanoimprinting and patterning of materials [20,21] etc. and has attracted much attention as a scalable and easily reproducible template method. The pore formation during the anodization process leads to nanopatterning of the underlying aluminum layer resulting in a structured Al surface after the selective removal of the AAO template, typically used as a guide for ordered pore formation in a double anodization process [12,22–24]. Moreover the influence of the operating conditions during the anodization process on the fabrication of AAO and the underlying aluminum pattern has been reported in literature [25–27]. However aluminum is an abundant and cheap material with interesting plasmonic properties [28,29] and little attention has been drawn on the optical properties of the underlying concave Al patterned surface resulting from the fabrication of AAO templates.

Here, we report an alternative, rapid and easily scalable fabrication method for light trapping aluminum nanostructures, using AAO templates on supported silicon (Si) substrates, avoiding thus the time consuming lithographic techniques [30] and long anodization processes of thick aluminum foils [31] as patterning methods. To demonstrate the light enhancement effect, we conduct a non-destructive dry topographic modification method of near-field mapping, based on local laser ablation of an “imaging” polymer layer deposited on the aluminum nanostructures [32].

2. Experimental

We used *p*-type silicon wafers (1–100 Ωcm, (100) crystal orientation) as substrates. After an initial cleaning process (15 min sonication in acetone, followed by 15 min sonication in isopropanol and nitrogen-based drying), 10 nm titanium (rate

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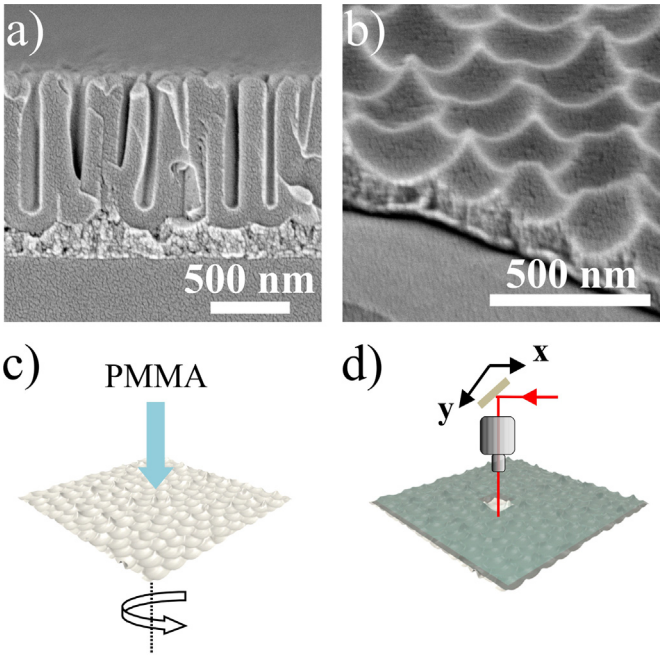

Fig. 1. Schematic illustration of the experimental process. (a) SEM image of an AAO template fabricated from phosphoric acid. (b) SEM image of the Al concaves of the sample in (a) after selective etching of the AAO. (c) PMMA spin-coating and (d) irradiation and direct observation via laser scanning microscopy.

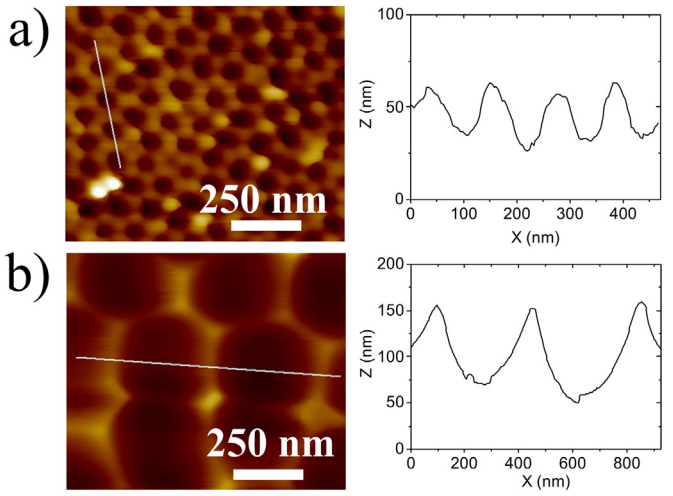

Fig. 2. In the left column, AFM characterization of aluminum concaves exposed after removal of the AAO in a mixture of chromic acid and phosphoric acid is shown. Samples have been anodized in oxalic acid in (a) and phosphoric acid in (b), while in the right column the respective concave profiles are shown for the two aformentioned electrolytes.

0.05 nm/s) and subsequently 800 nm of aluminum (rate 0.1 nm/s) were deposited via e-beam evaporation. The titanium layer serves as adhesion layer between the silicon and the aluminum layer. The silicon wafers were hand-cut with a diamond cutter into 20×20 mm^2 samples, followed by a rinse with isopropanol and blown dry with nitrogen prior to anodization. We performed the anodization of the aluminum substrates in a home-built Teflon container, with a cooling system (Brinkmann LAUDA RM 6), under potentiostatic control (Keithley 2400). The temperature of the substrate was maintained constant at 5 °C for all samples during anodization, while the potentials applied for samples in different electrolytes were 40 V for the 0.3 M oxalic acid and 120 V for the 5% phosphoric acid. Anodization times were $t=16$ min. for anodization in oxalic acid and $t=26$ min. for anodization in phosphoric acid. After the anodization of Al in different electrolytes, the AAO was etched selectively in a mixture of chromic acid (20 g/l) and phosphoric acid (70 ml/l) at constant temperature of 60 °C.

Directly after the removal of the AAO, a 200 nm thick poly (methyl methacrylate) (PMMA) layer was spin-coated on top of each sample's concave surface. This layer thickness turned out to be sufficient to fully cover all concave structures, while still remaining thin enough to be sensitive to the laser ablation experiments [32]. In order to obtain the required robustness for a dry ablation treatment, all samples were baked for 90 s at 200 °C.

Directly after PMMA coating, samples were mounted on a custom built laser scanning microscope (LSM) and raster scanned with a Ti:Sapphire laser beam (Spectra Physics Tsunami, sub 100 femtosecond pulses, rep. 82 MHz, max pulse energy ~8 nJ) with the central wavelength (λ) set at 790 nm. It is worth to notice that, due to the femtosecond regime of the used light pulses, we have eliminated all thermal effects, which could otherwise appear for longer pulses [33]. In Fig. 1, the overall fabrication process is presented, first the deposited aluminum is anodized to form the AAO template (a) and then the AAO template is etched away in a mixture of chromic acid and phosphoric acid to reveal the underlying aluminum nanostructures (b). A thin layer of PMMA is spin-coated onto the samples as shown in the schematic in (c) followed by the laser ablation experiments (d).

The ablation experiments were performed at normal incidence with linearly polarized light illumination. We scanned a focused laser beam via an objective lens ($\times 40$, Nikon) with a numerical aperture of 0.6, to ensure a nearly diffraction limited laser spot. The laser treatment results were monitored by a CCD camera system. The laser fluence and number of pulses per spot were precisely controlled and set below the PMMA ablation threshold, such that only on structured aluminum areas, exhibiting field-enhancing nanostructures, coatings would be ablated. For subsequent, precise imaging with a Scanning Electron Microscope (SEM – Hitachi S-4800), all samples were sputter-coated with a 3 nm thin layer of Au:Pd. Topography analysis of the nanostructured aluminum samples without any PMMA was conducted with an Atomic Force Microscope (AFM – Veeco Dimension 3100).

3. Results and discussion

Fig. 2 shows 2D AFM images of the aluminum concaves after selective removal of the AAO fabricated in different electrolytes.. The surface shows arrays of hemispherical dimples randomly arranged over the sample area, denoting that the height of the structures does not exceed the thickness of the spin coated PMMA layer. Samples fabricated from oxalic acid have an average concave size of 110 ± 20 nm, while samples fabricated from phosphoric acid have an average concave size of 300 ± 20 nm.

Fig. 3 shows, SEM images of aluminum concave samples after etching the AAO template fabricated from oxalic acid in (a) and from phosphoric acid in (b), respectively. It is worth mentioning that the dimple structures follow the same concave pattern as the bottom structure of the formed AAO. In (c) and (d) the ablated SEM images of the correspondent concaves from the different electrolytes in (a) and (b) are shown. It can be observed that ablation occurs on both samples and that the ablated area is located at a distinctive area of each concave structure, more clearly visible in (d) for concaves fabricated from AAO in phosphoric acid as larger structures give a better contrast. From (c) and (d) cracks and small voids on the PMMA layer are evident that are not related to the