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Fabrication of high aspect ratio (>100:1) nanopillar array based on thiol-ene

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ABSTRACT

Nanopillar arrays have attracted considerable attention lately based on confinement effects and large surface to volume ratios. In this study, we demonstrated an efficient low-cost method for fabrication of large-area high aspect ratio nanopillars based on thiol-ene. Anodic aluminum oxide (AAO) template with ordered deep hole array was employed as the master mold. The low-viscosity and highly rigid UV-curable thiol-ene polymer was used as the structure material. The deep holes were filled with the liquid thiol-ene by overcoming the surface tension. Upon curing under UV irradiation, the thiol-ene formed a rigid cross-linked polymer network. The thiol-ene nanopillars were achieved after releasing the AAO mold in the corrosive solution, due to the corrosive-resistance of the cross-linked polymer. Based on the novel method, we fabricated thiol-ene nanopillar array with the diameter of 296 nm and aspect ratio of higher than 100:1. The experimental results demonstrated that the properties of thiol-ene polymer were excellent and the fabrication method was feasible.

1. Introduction

Fabrication of nanostructures, especially high aspect ratio patterns such as nanopillars and nanowires, perform key functions in many technologies [1–3]. Due to allowing higher device densities, nanopillars have already been utilized in a broad range of applications in electronics [4,5], optics [6], chemical analysis [7], and sensors [8]. In particular, devices for high frequencies based on diffraction (e.g. Fresnel zone plates and diffraction gratings) and on refraction (e.g. wave plates and retarders) require both nanoscale dimensions and high aspect ratios for optimal operation. Therefore, ways to fabricate the high aspect ratio nanopillars in an economic, simple, large-area, and high-precision were desirable.

Two standard routes for nanofabrication are top–down lithography and bottom–up growth technique. The first route includes conventional photolithography, electron beam lithography (EBL) [9] and focused ion beam lithography (FIBL) [10] followed by plasma etching [11–13]. Y. C. Chan [14] fabricated silicon pillars as small as 300 nm in feature size with an aspect-ratio higher than 50 by deep reactive ion etching (DRIE). It was low efficient and high-cost. The second route by vapor–liquid–solid growth has risen in popularity as a low-cost alternative. The most common techniques are nanosphere lithography (NSL) [15–18] and block copolymer lithography [19,20]. Nanospheres or nanopaticles were introduced onto the substrate to create different nanostructures by self-assembly [21,22]. However, long-range order was still not achieved due to domain formation.[23] Besides that the diameter uniformity and growth rate differences led to inhomogeneities in the height for nanopillars.

Nanoimprint lithography (NIL) [24,25] has been demonstrated as a next generation lithography technology for low-cost and high-throughput sub-10 nm nanopatterning. S. Y. Chou [26] reported a wide-area fabrication of sub-50 nm diameter and high aspect ratio greater than 60:1 silicon pillar arrays by combing NIL and DRIE. L. J. Guo [27] presented a method to fabricate high-aspect-ratio polymer micro-/nano-structures (higher than 10:1) by the DEP-ECP-driven UV-imprinting process. However, the high-quality nanoimprint mold relied on the other lithography techniques that were complicated and expensive. It was also a challenge to release the mold for the high-aspect-ratio nanopillars. The aspect ratio of the nanopillars was severely limited by the physical and mechanical properties of nanoimprint resist.

The UV-curable thiol-ene, as one click reaction, has the advantages of rapid polymerization, low shrinkage, low viscosity, and high Young's modulus [28]. Due to the excellent mechanical and physical properties, thiol-ene polymer has been used widely as the nanoimprint resist in NIL to fabricate high-resolution nanostructures [29–31].

Herein, we propose a novel non-lithographic method for fabricating high aspect ratio nanopillars based on the thiol-ene polymer. The anodic aluminum oxide (AAO) template with uniform deep holes array was employed as the master mold, which was fabricated simply and with low cost. The thiol-ene polymer with low viscosity and high Young's modulus was used as the nanostructure material. The thiol-ene filled the deep holes of the AAO mold by overcoming the surface tension, and formed the cross-linked polymer network when exposed under UV irradiation. The thiol-ene nanopillars array was obtained after releasing the AAO mold in the alkaline solution. Using this method,

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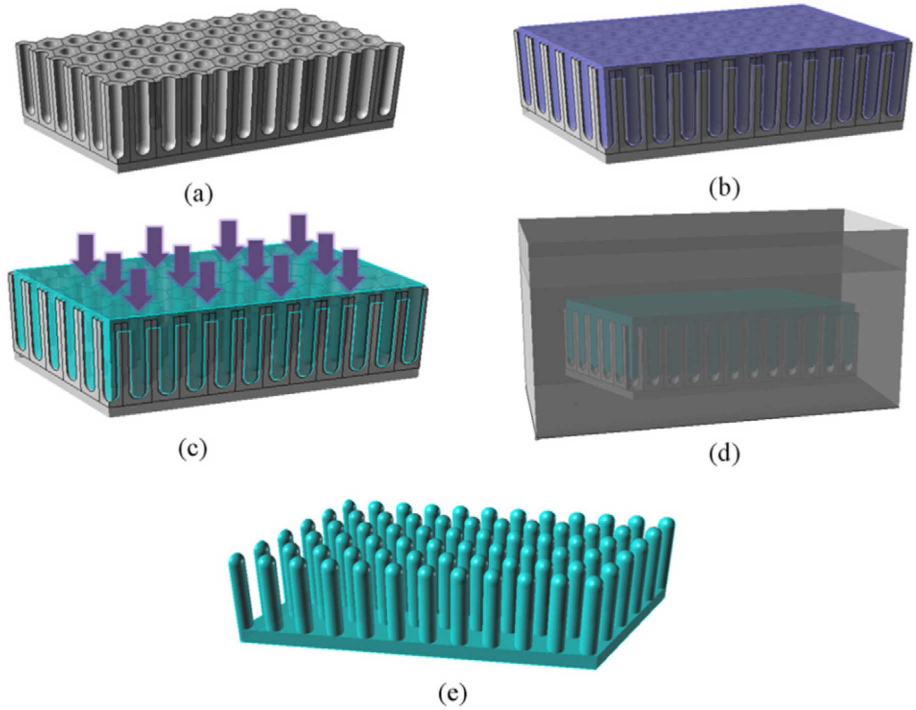

Fig. 1. Schematic of the fabrication process of the polymer nanopillar: (a) preparation of the AAO mold; (b) coating thiol-ene propolymer onto the AAO mold and filling of the deep nanopores; (c) exposure under UV irradiation and formation of cross-linked polymer network; (d) removal of the AAO mold in the alkaline solution; (e) final cross-linked polymer nanopillar array.

296 nm diameter and high aspect ratio (>100:1) thiol-ene nanopillar array was fabricated.

2. Experimental section

The approach to fabricate high aspect ratio nanopillars is shown in Fig. 1. An AAO template with uniform ordered holes array was firstly employed as the master mold as shown in Fig. 1a. The UV-curable thiol-ene polymer was then coated onto the AAO mold and filled into the deep holes by spinning and casting as shown in Fig. 1b. Upon curing by exposure to UV light, the thiol-ene polymer formed a cross-linked polymer network with features replicated from the master mold via a radical-mediated polymerization process as shown in Fig. 1c. As presented in Fig. 1d, the AAO template was dissolved in the alkaline solution and the cross-linked polymer was left. The thiol-ene nanopillar array was fabricated after cleaning with the ultrapure water in Fig. 1e. The size of the nanopillars was determined by the mold and the structure materials.

2.1. Fabrication of the AAO template

A Φ20 mm aluminum wafer with the purity of 99.99% was firstly annealed at 500 °C for 2 h to remove the internal stress. And the aluminum film was then electrochemically polished in a perchloric acid and ethanol solution (25:75) and cleaned in deionized water and acetone. Subsequently, the aluminum film was treated via a two-step anodic oxidation process [32]. The polished aluminum was put into 0.4 M sulfuric acid at 0 °C and anodic oxidation took place with a voltage of 25 V for 2 h. Then the sample was put in a mixture of solutions of phosphoric acid and chromic acid to remove the alumina layer and rinsed in deionized water. Subsequently, the sample was under anodic oxidation for 2 h in the same conditions. Secondary oxidation of the AAO took place with 0.3 M phosphoric acid for 25 min, and then the sample was rinsed into deionized water and dried by nitrogen. The resulting AAO template had an average diameter of 300 nm and a height of >30 μm, and a hole density of about 1010 cm^{-2} was achieved, as shown in Fig. 2.

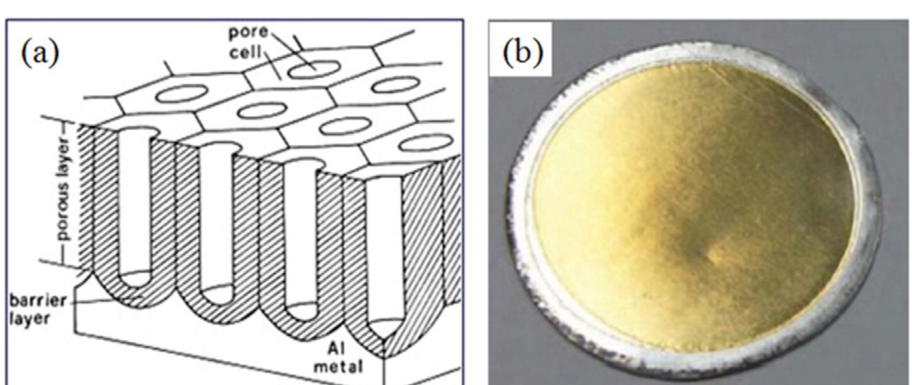

Fig. 2. AAO template was fabricated: (a) the sketch map of the AAO structure; (b) the photo of the sample.