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Fabrication of large-scale periodic silicon nanopillar arrays for 2D nanomold using modified nanosphere lithography☆

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Abstract

We present a fabrication procedure that can form large-scale periodic silicon nanopillar arrays for 2D nanomold which determines the feature size of nanoimprint lithography, using modified nanosphere lithography. The size of silicon nanopillars can be easily controlled by an etching and oxidation process. The period and density of nanopillar arrays are determined by the initial diameter of polystyrene (PS) spheres. In our experiment, the smallest nanopillar has a full width half maximum (FWHM) of approximately 50 nm, and the density of silicon pillar is $\sim 10^9/cm^2$. Using this approach, it is possible to fabricate 2D nanoimprint lithography mask with 50 nm resolution.

Keywords: Silicon nanopillar; Modifiled nanosphere lithography

1. Introduction

In recent years, nanoscale structure achieved by self-assembly process has received much attention because of their unique properties and potential applications in photonic crystals [1,2], optoelectronic devices [3], catalysis [4], data storage [5] and so on. There are many techniques available for the formation of periodic arrays of nanostructure, such as electron-beam lithography [6], micro-contact printing [7], electrochemical etching [8], as well as X-ray lithography [9]. Although these lithography techniques can be used to control the morphology of the arrays to a certain degree, high-cost and sophisticated processes limit their usefulness. Therefore, much research effort has been focused on the development of low-cost, high-throughput, high-resolution lithography techniques for both industrial applications and fundamental studies. Among these approaches, nanoimprint lithography is one of the most promising schemes. It has been proven [10,11] that the nanoimprint lithography techniques can fabricate large-scale nanostructures however, there are still technical challenges to be solved, such as the nanomold preparation for nanoimprint. It is fabricated by electron beam lithography, which limits the accessibility of nanoimprint lithography. In this paper, we present a simple mold fabricatiom technique using modified nanosphere lithography.

Deckman's nanosphere lithography [12] is a well-know method to fabricate large-scale nanostructures, which encompass all the fundamental advantages of self-organization. This technique makes use of PS spheres to form large single or double layer, close packed arrays driven by capillary forces. This single or double layer then works as a deposition mask. After metal deposition and subsequent lift-off, large-scale triangular nanoparticles can be obtained. Since nanoparticles are formed by filling the voids between PS spheres, which are in physical contract, it is very difficult to change the size of nanoparticles and their spacing. To solve this problem, we modify this nanosphere lithography process. First, we propose to transfer the single mask formed by the self-assembly PS spheres into silicon substrate by reaction ion etching (RIE) with CF_4 to produce silicon nanopillar. After the pattern transfer process, the size of the nanopillars can be reduced by oxidation and etching process. Therefore, the size of nanopillar and the spacing can be improved easily. By this modified nanosphere lithography, we fabricate a 2D mold of large-scale, well-ordered, periodic nanopillars for nanoimprint lithography.

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2. Experimental section

2.1. Mask formation

The PS spheres in our investigation were purchased from Duke Scientific Corporation as 10% by wt. in solution with standard deviations between 5% and 7%. And the mean diameter of PS sphere is 220 nm. The substrates were p-type (1 0 0) crystalline silicon. Prior to being used, silicon substrates were cut into pieces of 10 mm × 10 mm. Each square was thoroughly cleaned with standard RCA I process, that is, a treatment with a 1:2:6 solution of NH_4OH (25%), H_2O_2 (30%) and water at 80 °C for 15 min. This created a flat, hydrophilic silicon surface.

A large monolayer of PS spheres with highly ordered areas (more than 1 cm^2) were obtained on water surface by self-assembly method [13]. Such monolayer was then lifted off the water surface to the previously mentioned silicon wafers. The substrates coated with monolayer PS films were then dried in air at room temperature. After being dried, these substrates were annealed in an oven for 1 h to consolidate the spheres and bond the monolayer to the substrate tightly at 80 °C, which being lower than the glass-transition temperature of the PS sphere. Such annealing forms an area contacted, instead of a point contract between the PS spheres and the silicon substrate. Obviously, it was of benefit to increase the binding force between PS spheres and the silicon substrate. Finally, these substrates with PS mask could be used as a mask in the next RIE process.

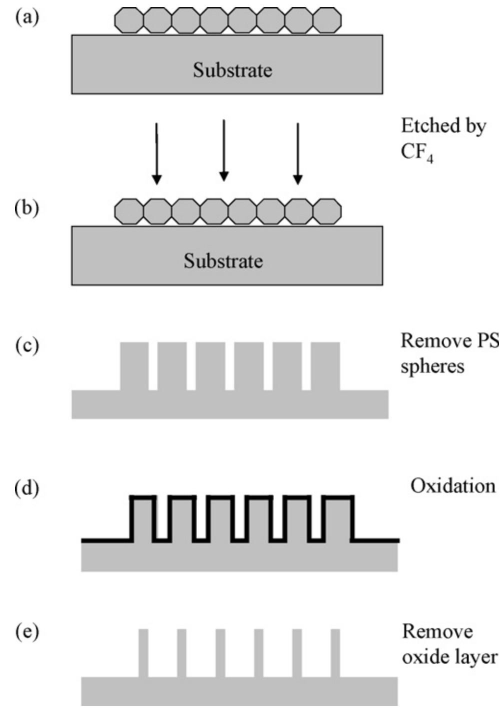

Fig. 1. Schematic of the fabrication of large-area periodic nanopillar for 2D nanomold by a single layer mask of PS spheres using modified nanosphere lithography. (a) The silicon substrate is coated with a single layer of PS spheres. (b) The substrate is etched by CF_4. (c) After removing the PS spheres, periodic nanopillar arrays are formed. (d) The sample is oxidized in an oven to produce oxide layer. (e) The size of nanopillars can be reduced by removing the oxide layer.

2.2. Nanopillar formation

Our approach to nanopillar formation using modified nanosphere lithography includes a three step process. The fabrication producer is outline in Fig. 1. In the first step, the prepare silicon substrate with PS sphere as mask was etched by RIE. Etching was done using CF_4 (40 sccm) at 40 w for fixed etching times. In this RIE process, the etching rate of silicon with carbon fluoride is bigger than that of PS sphere. So, the PS sphere works as an etching mask or templates, and the nanoscale silicon pillars are formed after RIE in the silicon substrate. The second step of fabrication process was thermal oxidation. After the PS nanospheres were removed in a solvent such as methanol or tetrahydrofuran (THF) with ultrasonic application, the substrate with silicon pillar was loaded in an oven which purged with pure oxygen at 1000 °C, to produce a layer of silicon oxide on the surface of pillar. The thickness of oxide layer can be controlled by the oxidation time. The last step of fabrication process was peel-off of oxide layer. In this process, the oxide layer was removed in a buffered HF solution, and then silicon nanopillars with smaller lateral diameter can be obtained.

3. Results and discussion

We used SEM and AFM measurement to investigate the structure and the morphology of the silicon nanopillars. The SEM measurement was performed on LEO1530VP. And the AFM measurement was performed on Nanoscope III (Digital Instrument, USA). SEM image of the periodic arrays of single layer PS spheres with diameters of 220 nm is presented in Fig. 2, which displays a classic honeycomb structure of the PS mask. In addition, the inset image gives the corresponding fast fourier transform (FFT) pattern, which confirms that the

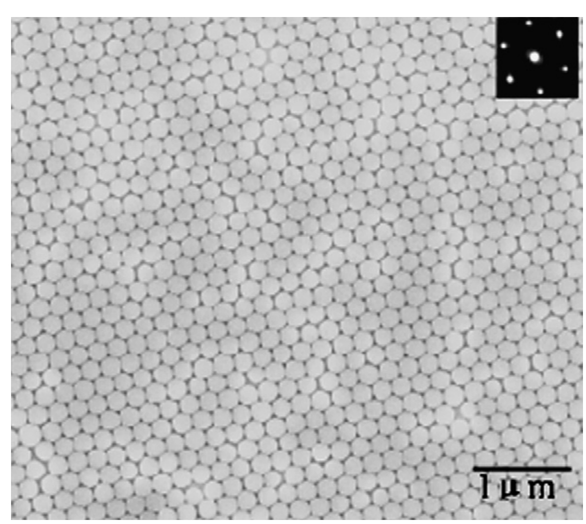

Fig. 2. SEM image of single layer PS spheres. The inset image is the corresponding fast Fourier transform (FFT) pattern.