Irregular shaping of polystyrene nanosphere array by plasma etching

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The morphology of nanospheres is crucial for designing the nanofabrication in the nanosphere lithography. Here, by plasma etching, the controllable tailoring of the nanosphere is realized and its morphology dependence on the initial shape, microscopic roughness, and the etching conditions is investigated quantitatively. The results show that the shape evolution strongly depends on the etching gas, power, and process duration. Particularly, the aspect ratio (diameter/height) significantly increases with violent etching, turning the spherical shape into tiny ellipsoidal nanoparticles. The findings are practical to the protocol of non-uniform etching of nanoobjects and provide the useful design tool for the device fabrication at nanoscale.

Keywords: polystyrene; nanosphere array; self-assembly

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1. Introduction

As the fabrication techniques of electronic devices are currently switching from microscale into nanoscale, both traditional and novel techniques have been well developed. Optical lithography [1], for example, which strongly depends on the special photomask for diverse micro/nano devices, has been extensively used in semiconductor industry. In order to avoid the using of masks, atomic force microscope (AFM) [2] was designed to manipulate and fabricate the structures down to the nanoscale. By moving the ultrasharp tip, it easily patterns the material into desired structures directly, through either physical control or chemical reaction, however, the technique has its limitations due to reliability and time cost. The maskless methods, such as focused ion beam (FIB) [3], electron beam lithography (EBL) [4] and proton beam writing [5] are accurate and flexible but usually suffer from the high cost and long production time. Nanosphere lithography (NSL) [6], as a low cost, large-area, novel material nanofabrication technique, based on the self-assembly of nanoparticles into the well-ordered mask, is employed to manufacture versatile nano- and micro-structures, such as micro-electromechanical systems (MEMS) [7, 8], photonic crystals [9, 10], memory devices [11, 12], etc. NSL allows low-cost and controllable nanofabrication, thus attracting tremendous attention.

In the NSL, the periodic particle array (PPA) made from latex (i.e. polystyrene spheres) is primarily functioned as a pre-mask, and can be readily realized via methods such as capillary deposition [13], spin-coating [14], interface assembly [15], etc. Usually, the close-packed nanosphere array is produced by these self-assembly methods, which requires the pattern transfer from hexagonal configuration to other desired structures, such as triangular, rectangular, circular dot array etc.,
subsequently limiting the NSL for versatile structure fabrication. During the transformation of the close-packed template to the final structures, shaping individual nanospheres by heating [16, 17] and etching [18, 19] plays an important role. Heating leads to the melting of the soft spheres PPA, then shrinking or deforming into the netlike structure, which tunes this 2-D array. In contrast, the etching method aims to adjust the size of the individual sphere. C. Cong et al. [17] designed the regular holes with rectangular and circular shapes by both heating and etching, and also obtained necklike structures by plasma etching. As reported by Y. H. Ting et al. [20], Ar/O\textsubscript{2} was used to etch the polymer film to study the effects of the aggregation and cross-linking diblocks of polymer films on surface roughness. By examining the optical properties of PPA nanospheres, T. Fujimura et al. [21] observed the irregular modification of polystyrene (PS) nanospheres (aspect ratio \( \neq 1 \)) during the reactive ion etching, and found that this symmetry-breaking affected the optical properties of the nano-array. When manufacturing hierarchical nanoparticle arrays, D. Xia et al. [22] observed, with a scanning electron microscope (SEM), the etched PS spheres which had a rough top and elliptical shape. As the uniformity of the sphere array and the controllable shape of the individual spheres are highly desirable for device applications it is important to understand the etching process for the nanosphere template or mask made from the nanospheres arranged in the well-ordered way. Although the PPA has been developed by various self-assembly methods and etching processes, the shape evolution of the sphere by tailoring morphology (i.e. aspect ratio) has not been well investigated so far, and the anisotropy (i.e. sphere or ellipse) has not been widely discussed as well. Moreover, the refined surface roughness of the nanosphere after shaping needs to be examined quantitatively.

In this work, we investigate the effect of process parameters such as plasma etching power, gas flow, substrate material, type of etching gas, on the shape and roughness of a nanosphere. By varying systematically the key parameters, the dependence of the diameter to height ratio of the nanosphere on the etching conditions is established.

2. Experiments

2.1. Self-assembly of PAA template

Before the etching process, spheres of nanometer size were initially spread onto a substrate to obtain close-packed monolayer coverage. The polystyrene sphere is a good candidate for plasma etching, due to its polymer nature, commercial accessibility, and the wide range of applications in the NSL technology. Aqueous suspension of polystyrene nanospheres (10 \% w/v in concentration, 762 nm in diameter, GmbH, Germany) were nicely monodispersed (coefficient variation < 5 \%) and used as received. Note that the monodispersity of nanospheres is a key factor to produce the uniform 2D colloidal crystal layer, and significantly influences the quality of the nanosphere array during the etching process. The solid content of the colloidal solutions was diluted to about 5 \% w/v by adding ethanol. The solution drop was introduced onto the air/water interface vertically by using a pumping syringe. In this process, the drop of solution should be located just above the air/water interface, considering the fact that pushing the solution drops onto the interface leads the suspension and water surface to merge. Then the nanospheres spontaneously spreaded along the air/water interface and aggregated into a regular close-packed structure. In our case, the nanospheres were taken apart from each other, in order to measure their dimensions in the AFM system. Thereafter, clean silicon and glass substrates were covered by the nanosphere monolayer film by picking up the nanosphere film floating at the interface.

2.2. Plasma etching

Subsequently, the dry nanosphere films were transferred into a plasma system (FEMTO Beispiel Variante A, Diener, Germany) and etched under different conditions. The dielectric constant of the substrate affected the local electric field between two electrodes of the plasma system, thus possibly causing variation in the etching process. Consequently, two substrates were selected to support the nanospheres, i.e. glass and silicon substrates. During the plasma etching, the influence of gas type