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Ordered nanostructures array fabricated by nanosphere lithography

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Abstract

Ordered PS array was deposited on the silicon substrate and the rigid monolayer formed due to the interconnection by the sodium dodecyl sulfate. Metal film with nanoholes was fabricated by depositing the film onto the PS array. Co nanorings were fabricated in the following Ar ion etching process masked by PS particles. Silicon-based nanoholes were also fabricated by RIE process after the removal of the PS particles by chemical solution. The diameter of PS particle was thinned by the O_2 etching process, and thus it is possible to control the diameters of the nanorings and the nanoholes.
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1. Introduction

The nanosphere lithography attracted recent attentions for successful fabrication of ordered nanostructures over large areas [1–3]. In this process the latex particles self-organized into ordered pattern first, and then 2D array was obtain by depositing the desired material onto the ordered colloidals [4–6]. Bartlett et al. prepared highly ordered, 3D macroporous magnetic networks based on the polystyrene template and the results revealed the higher coercivity and irreversible field than non-templated samples of the same film [7]. The colloidal arrays were also used to prepare other nanostructures for optical purpose, such as nanotubes and hollow metal nanostructures [8,9]. In some cases spherical particles do not satisfy all the usage of the colloidal particles [10]. Choi et al. developed a colloidal lithographic approach to the fabrication of non-spherical colloidal particle array with a long-range order by selective reactive ion etching (RIE) of multilayered spherical colloidal particles, which provided new types of functionalities that would not be given by spherical particles, widening the applying scope of nanosphere lithography [11,12]. Several methods were suitable for the colloid monolayers, such as Langmuir–Blodgett [13], spin-coating [14–16], and self-assembly method [17,18]. In this paper we fabricated 2D polystyrene latex array on decorated silicon wafer surface by the self-assembly technique, and then ordered nanostructures were prepared, including Co nanodots, Co nanorings, holed Au film and silicon-based nanoholes.

2. Experimental

The 200 nm monodisperse polystyrene particles were purchased from Duke cooperation (10 wt% aqueous solution). And the detailed process for self-organization was reported in our previous jobs [19]. In brief, the diluted polystyrene solution was applied onto the modified substrate, which spread all over the substrate. The wafer was then slowly immersed into the glass vessel filled with water and polystyrene particles started to an unordered monolayer on the water surface. The addition of sodium dodecyl sulfate solution was dipped onto the water surface and drove the monolayer into highly ordered pattern. Such monolayers were then lifted off by the decorated silicon wafers. The RIE process was performed on magnet enhanced reactive ion etching system (MERIE, ME-3A mold, China). The Co and Au film were deposited in a magnetron sputtering system. The base pressure was 4×10^{-5} Pa and the argon pressure was 0.4 Pa during deposition. Ar was used to etch Co and CF_4 was used to etch Si

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substrate. The SEM measurements were performed on LEO1530VP. And AFM measurement was performed on nanoscope III, tapping mode.

3. Results and discussion

3.1. Formation of 2D ordered colloidal array

The addition of sodium dodecyl sulfate solution was important for the formation of 2D ordered colloidal array. PS colloidals can float randomly on the water surface due to the surface strain in spite of the little larger density, and the pattern showed no obvious long-range order (Fig. 1a) The addition of the sodium dodecyl sulfate solution changed the PS array into a dense hexagonal packing pattern over 1 cm^2, and the inset image gave the FFT pattern showing long-arranged order (Fig. 1b). In some places the larger particles disturbed the particles around and the ordered pattern was distorted, showing the monodispersed colloidals are necessary for perfect superlattice structures in this process. The addition of the sodium dodecyl sulfate solution

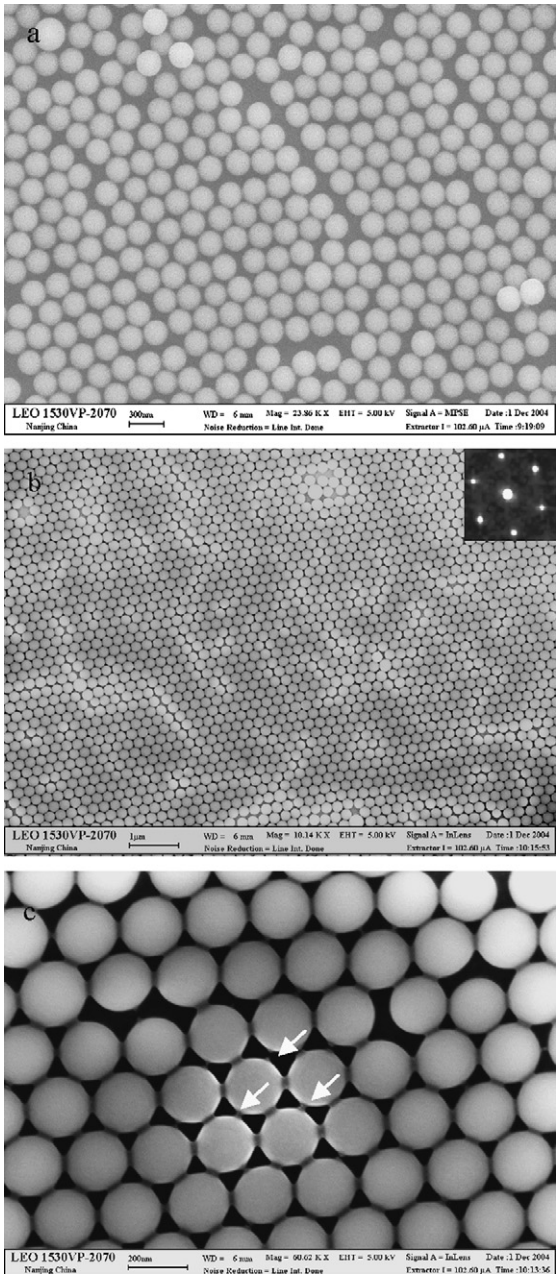

Fig. 1. The PS scattered on the water surface due to the surface stress (a); then the addition of the sodium dodecyl sulfate solution drive the particles together (b); the solid sodium dodecyl sulfate connected the neighbor colloids firmly and the pattern was maintained even when transferred from one substrate to another (c).

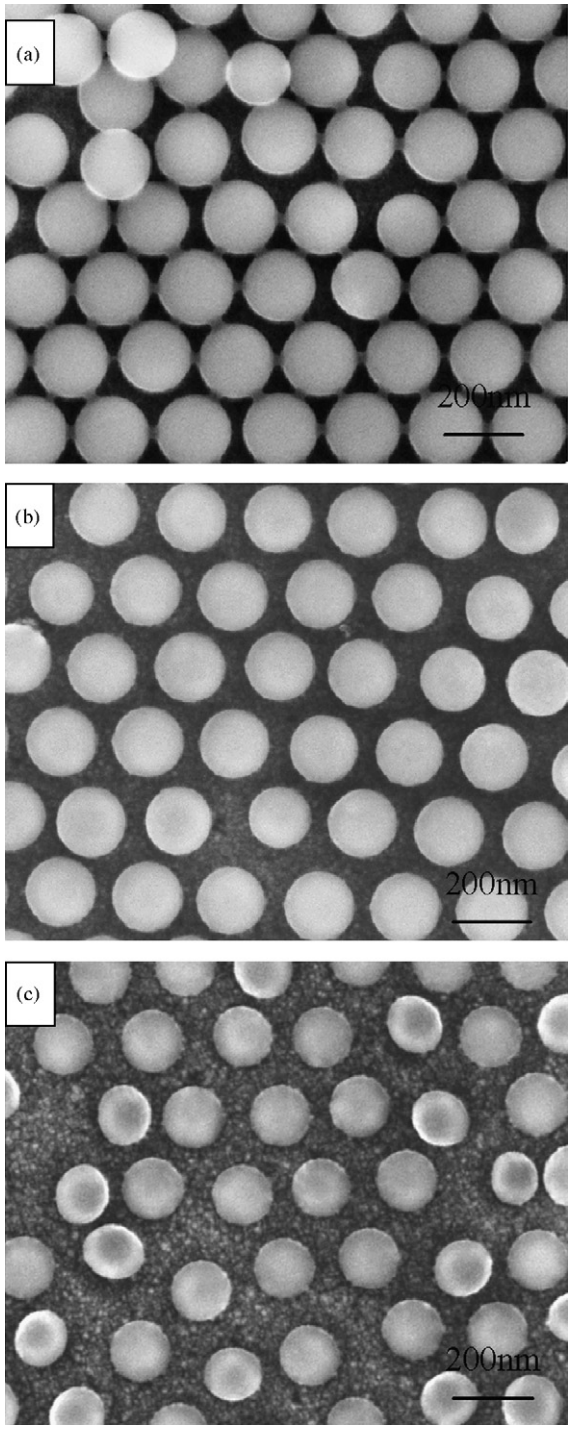

Fig. 2. SEM images of the PS latex thinned by oxygen: 0 s (a) 30 s (b) 45 s; (c) 60 s.

was important for the formation of the ordered PS array. The solution spread on the water surface and pushed the particles together, working in the similar way to the bar used in the LB technique. We re-floated the PS film onto the water surface by immersing the sample into water and the structure of the film was even maintained when the superlattice was transferred onto a new silicon substrate. The magnified image showed that the sodium dodecyl sulfate worked as an interconnecter, which made the pattern rigid (Fig. 1c).

We applied oxygen RIE to the polystyrene beads at 16 mW/cm^2 and no obvious changes happened to the arrangement and the shapes of the polystyrene beads. The diameters decreased with the etching time as reported in our previous work [19]. The diameters were decreased to 190 nm, 180 nm and 160 nm for the etching time 30 s, 45 s and 60 s, respectively (Fig. 2). The thinned polystyrene diameter D and the oxygen etching time t obey the following empirical equation:

$$D = D_0 \cos\left(\frac{\arcsin kt}{2D_0}\right)$$

Here, D_0 is the initial diameter of the polystyrene beads and k is the constant depending on the etching conditions such as pressure, incident power, temperature, and so on. When we choose $k = 4.0$ empirically, the experimental data agree well with above formula. According to equation mentioned above, we can get the desired bead sizes by controlling the etching time.

2D ordered latex particle arrays are excellent opals [16,17]. In our previous works, silicon pillars with controllable diameter were fabricated with the PS masking effect. And the structural color phenomenon was observed [19]. The colloidal arrays were also used to prepare other nanostructures for optical purpose, such as nanotubes and hollow metal nanostructures [8,9]. We deposited Co film onto the ordered PS array. Then PS particles were etched away by tetrahydrofuran and the fillings between the particles were left. The SEM images showed the Co film between colloidals form hexagonal array pattern and the single Co dots had quasitriangular shape (Fig. 3). Similar structures were obtained for Ni metal by other group and ordered carbon nanotubes were obtained. In another experiment magnetic nanodots of bilayer was fabricated by the method mentioned above and interesting magnetic properties were observed [20].

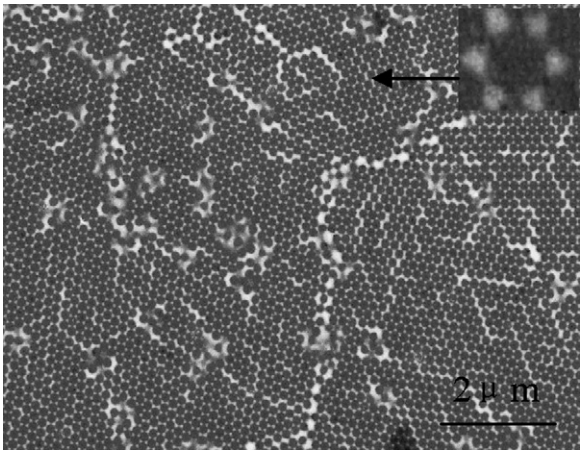

Fig. 3. The removal of the masking PS array left the triangular Co nanodots on the silicon substrate in hexagonal pattern.

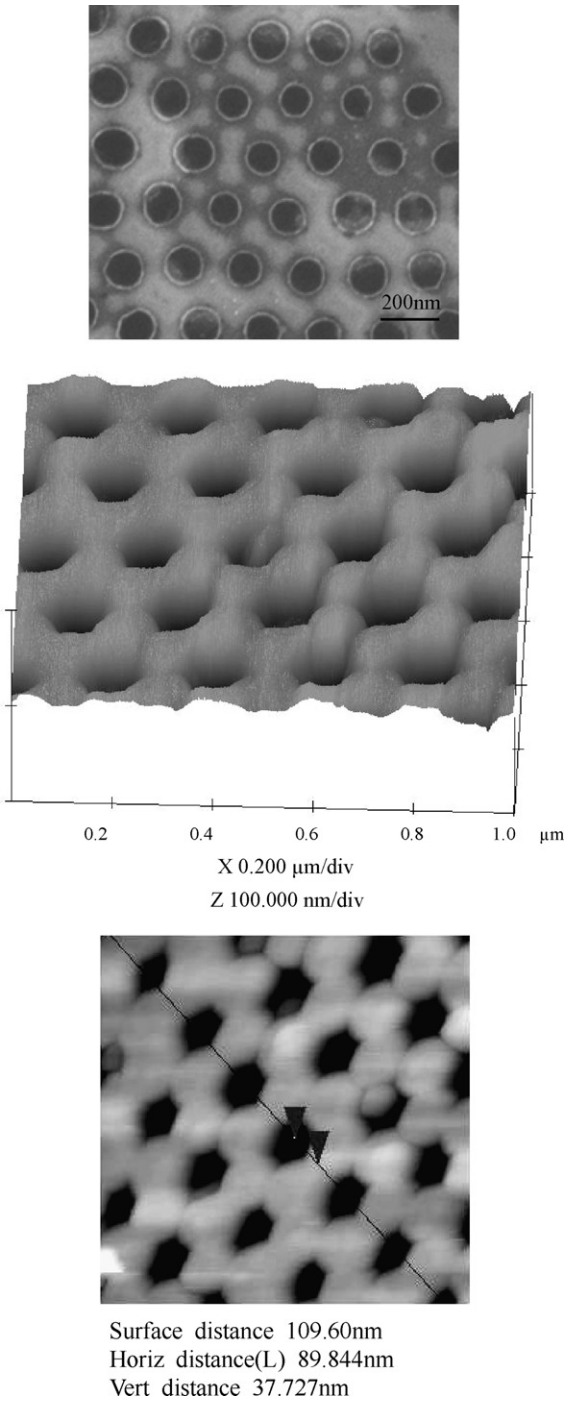

Fig. 4. The removal of the PS particles showed the porous Au film on the silicon wafer (a). AFM analysis showed the following etching process fabricated Si-based nanoholes at the exposed spots and the etched depth was 38 nm for 10 min, much slower than usual 80 nm/min (b and c).

3.2. Nanoholes based on ordered PS array

According to recent investigations, nanoholes found various applications in sensors, memories, measurement and so on

[21–24]. The researches also showed that the sub-wavelength holes in thin metal films act as point-like surface plasmons sources at normal or near-normal incidence. And the periodic nanoholes in metallic thin films worked as the structures for applications in photonic circuits and light manipulation at the sub-wavelength range. The arrays of nanoholes increased the transmission of light by orders of magnitude when the surface plasmons resonance condition was achieved, which was explored for applications in several relevant fields, ranging from quantum information processing to nanolithography. And the periodic arrays of nanoholes in ultrathin Au films were used as substrates for enhanced-Raman spectroscopy in the optical range.

In our experiment Au film was deposited onto the ordered PS array in the magnetron sputtering system. The removal of the PS particles left the ordered nanoholes in the gold film as shown in Fig. 4a. The periodicity of the holes agreed with the colloidal diameter. The boundary of the hole was a little thicker owing to the large local stress. RIE operation was performed to the sample for 10 min at 20 W. Fig. 4b shows the nanoholes into the silicon wafer after the removal of the gold film. The AFM measurement showed the depth of the hole was around 38 nm. In the another experiment no mask was used and the corresponding measured etching rate was around 80 nm/min. So the tiny exposed area limited the etching rate efficiently.

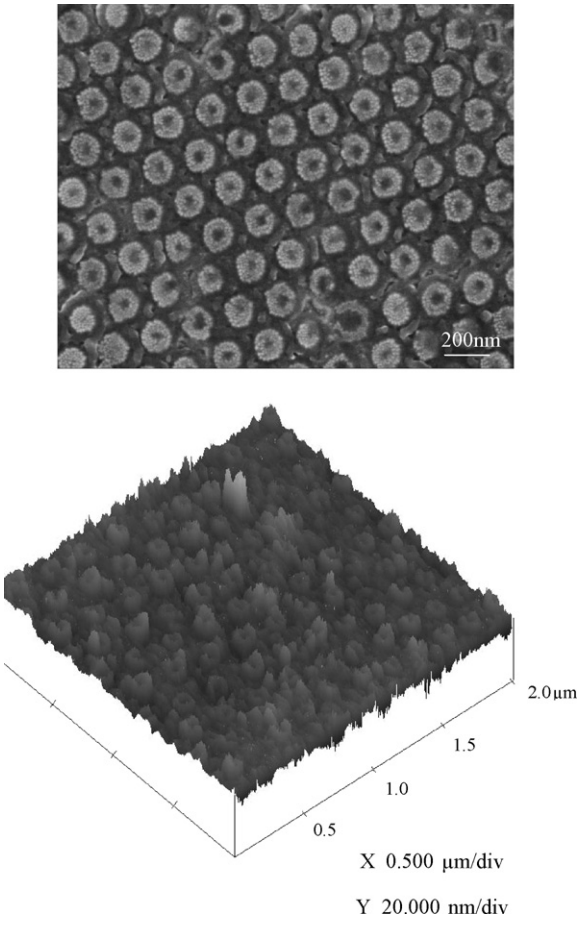

Fig. 5. SEM and 3D AFM image of Co nanorings fabricated on silicon substrate.

3.3. Co nanorings based on ordered PS array

Nanorings attracted intensive attentions recently for the potential applications in nanometer-scale sensors, resonators and transducers, and provided a unique test bed for studying piezoelectric effects and other phenomena at the small scale [25,26].

Recent researches revealed the potential applications of magnetic nanorings in the magnetic recording because the vortex state lowered the cross-talk between entities and reduced stray fields. For practical applications the ordered nanorings of magnetic materials were the next focus. We fabricated the ordered Co array based on the PS superlattice. After thinning the PS beads for 45 s, Co metal was deposited onto the PS covered substrate, and then Ar etching was applied. 30 min later tetrahydrofuran and oxygen etching was applied in turn to clean the PS residuals completely. SEM measurements showed Co nanoring arrays in long-ranged order with the external diameter 160 nm, hole diameter 100 nm and the thickness 25 nm (Fig. 5). The 3D AFM image also showed the clear ordered ring patterns. The diameters of these nanorings were controllable by etching the PS for set time.

The latest researches showed that the asymmetrical magnetic nanorings allowed more of the nanorings to end up in vortex state, meaning they have no stray field at all [27]. By tilting the substrate the asymmetrical nanorings are not difficult to prepare.

4. Conclusion

Ordered PS arrays were fabricated on substrate, which were used as mask in the following nanostructure fabrication process. Co nanodots, nanorings, and silicon-based nanoholes were prepared with the PS mask.

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