PATTERNED PERIODIC NANOPARTICLE ARRAYS BY MEANS OF ELECTRON BEAM IRRADIATION TO POLYSTYRENE NANOSPHERES

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Introduction

Nanospheres are colloidal particles that can be self assembled on solid substrates to create mono or multiple layers of colloidal crystals. This type of colloidal layers has found a wide range of applications, for example, in nanosphere lithography (NSL)[1–3].Within a close-packed colloidal layer, there is an ordered array of voids. Using the colloidal layer as a mask, one can deposit materials onto predefined locations onto the underlying substrate. The deposited material appears as triangular islands once the polymer spheres are removed by dissolution into a solvent.

Recently, there has been a growing interest in the formation of more complex structures via the modification of a preformed colloidal layer by reactive ion etching (RIE),[3] thermal annealing,[4] e.g., as well as directed assembly where the spheres are assembled onto patterned substrates.[5] Modification to the closed-packed colloidal layer, as demonstrated with RIE[5] opens up many new possibilities for the nanosphere-based lithographic technique.

We have recently studied the interaction of focused electron beam with polystyrene spheres on a silicon oxide surface, and found that exposure to electrons causes a significant shrinkage of the polystyrene spheres, without causing any damage to the silicon oxide substrate. It is possible to change the spheres diameter and shape accurately by controlling the electron dosage, thus fine-tuned the property of the mask.

Experimental

Materials

Silicon substrates were cut into 1×1 cm^2 in size from a silicon wafer and cleaned in acetone and deionized water for 1 hour each in an ultrasonic bath. Polystyrene nanospheres of 500 nm in diameter, purchased from Agar Scientific U.K, were either drop-coated or spin coated on the substrate to get a uniform single layer. When the liquid has completely evaporated, we obtained a single layer of spheres on the silicon oxide substrate.

Apparatus and Procedures

All atomic force microscopy (AFM) images were collected in ambient conditions with a Veeco Dimension 3100 AFM. Etched Si nanoprobe tips, with resonance frequency between 250 and 280 kHz were used in tapping mode to acquire the images. The scanning electron microscopy (SEM) images were obtained using a Philips FEI XL305FEG SEM, in a vacuum of 4×10^{-7} mbar, with acceleration voltages from 2 kV to 20 kV to be used as radiation source.

Results and Discussion

Figure 1(a) shows a single layer of nanospheres covering an area of 2 μm × 2 μm. We then zoomed into the sphere in the middle, Figure 1(b), and exposed this sphere to a lengthy period of electron beam exposure. During this exposure to a 5 keV electron beam, the contact area between two adjacent spheres was found to gradually decrease as shown by the sequence of images in Figures 1(b–e).

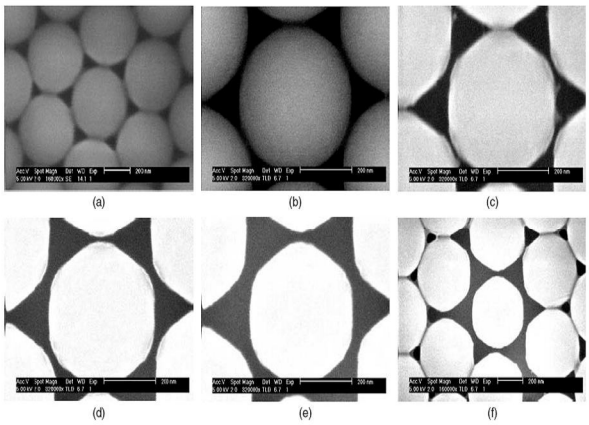

Fig. 1 Shrinking of the polystyrene sphere as a result of electron beam exposure at room temperature.

During the exposure, the electron beam was rastered over the entire area of the images. Following an exposure of 9.9 mC/cm^2, the sphere in the middle is seen to be detached completely from its neighbours, as shown in Figure 1(e). By comparing the images shown in Figure 1(a) and that in Figure 1(f), it is found that the diameter of the sphere has decreased, from its initial value of 500 nm to 435 nm following exposure to the electron beam, a reduction of 13%. These results have been published elsewhere.[7]

The shrinkage of the polystyrene spheres is likely to be caused by electron-induced damage of the polymer chains, resulting in partial loss of hydrogen and the formation of amorphous carbon-like structures, which could be insoluble to a particular solvent.

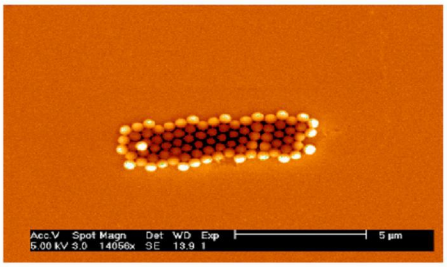

Fig. 2 A rectangular island of irradiated nanospheres.

Figure 2 shows a rectangular island of irradiated nanospheres after the spheres in the surrounding are removed by ethanol. Therefore, in addition to the shrinkage of the particle size, exposure to electron beam also changed the chemical properties of the spheres by altering their solubility in organic solvents.

Figure 3 a(1)-(2) are images of the nanospheres before been exposed for more than 5 minutes to electron beam radiation. Using blinker and expose technique, certain area of nanospheres was irradiated with electron beam for more than 5 minutes at higher resolution imaging, therefore the irradiated nanospheres were found to be manipulated and insoluble to ethanol. When gold is deposited onto this sample, we found that the ordered array of metal dots only forms in regions without the deliberate electron beam exposure as shown in Fig. 3b(1) and b(2).

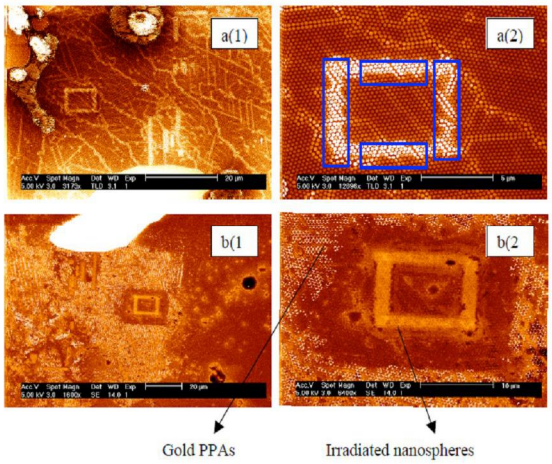

Fig. 3 a(1) and a(2) irradiated nanospheres before gold deposition. b(1)and b(2) were obtained after deposition of gold and removal of the spheres.

CONCLUSION

In conclusion, we have investigated the effects of electron beam exposure to polystyrene spheres organized on a silicon oxide substrate. We have demonstrated that both the size and the shape of the spheres can be changed with electron beam exposure. Furthermore, the surface chemistry of the spheres can be modified by electron beam exposure such that they become insoluble to organic solvent. The mask created from irradiated and non-irradiated nanospheres can be used to precisely pattern periodic nanoparticle arrays.

ACKNOWLEDGMENT

We thank UTHM for its financial support.

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