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Fabrication of integrated patterns using lithography and particles assembling techniques

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Abstract

This paper describes both physical and chemical techniques of nanoparticle assembling on a substrate pre-patterned by optical lithography or soft UV nanoimprint lithography. Integrated patterns of mono dispersed particles can be achieved by capillary forces, whereas functionalized particles could be assembled into holes of a metallic layer by chemical processing. To demonstrate the applicability of the methods, the fabricated patterns were transferred into a UV curable resist or a silicon dioxide layer by reactive ion etching. In addition, particles assembled into a microfluidic channel were used as artificial gel to show the feasibility of stretching single-strand T4 DNA molecules.

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1. Introduction

Mono dispersed micro and nanoparticles can be made of different materials such as silica, gold and polymers, and functionalized with various bio-molecules. On one hand, these particles are widely used for chemical and biochemical processing such as chromatography, biological imaging, cell capture, organic solid phases syntheses, etc. [1–3]. On the other hand, they can be manipulated by different physical and chemical means such as optical tweezers, magnetic, electric or dielectric forces as well as microfluidic flows [4–6]. From a research strategy point of view, it is highly interesting to use them to generate integrated devices by combing lithography and particle assembling techniques.

The pattern formation of nanoparticles on a substrate can be controlled by competing molecular interactions like hydrophobic versus hydrophilic components, gravitational,

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Van der walls, or Columbic interactions. This leads to the formation of different patterns [7–9], but remarkably, the most of the previous work for assembling particles of sizes in the range from a few to a few 100 nanometers were based on capillary forces. If a droplet of the particle solution is dried slowly on an unpatterned surface, the particles aggregate at the rim of the droplet because of attractive capillary forces between the particles when the water film thickness is in the dimension of the particle diameter. In order to form complex and well controlled systems, patterned arrays of templates fabricated in thin films of photo resist using conventional lithography can be used. By combining templates and capillary forces, nanoparticles can grow with unusual crystalline order and orientation. Chemically patterned substrates can also be used to obtain assembling organization. For example, functionalized nanoparticles can be absorbed on the pre-treated substrate via chemical reaction. In this work, both physical and chemical techniques have been studied in order to achieve a nanoparticle pattern formation that can be used in integrated devices. To cover a wide range of application fields, templates with micro and nanometer features were obtained on PDMS

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and glass substrates by using either optical lithography or soft UV nanoimprint lithography. In addition, the assembled particles could be successfully transferred into a photo curable resist layer or into the under layer substrate by using reactive ion etching techniques. Finally, we showed preliminary results of single strand T4 DNA molecules stretching in a microfluidic channel with self assembled silicon dioxide particles.

2. Experimental

2.1. Substrate pattern fabrication

The templates for particle assembling used in this work were fabricated by either optical lithography or soft UV nanoimprint lithography. For large sizes, patterns were generated into a thin film of photoresist spin-coated on silicon substrates using conventional contact mode photolithography with rigid chrome mask. Typically, a uniform thin film of positive photoresist AZ5214 was spin coated (4000 rpm, 60 s) on the substrate with a thickness of 1 µm. After exposure to the UV light and development, the surface was treated with trichloromethylsiloxane (TMCS) for anti adhesion. Then, the resist patterns were transferred into PDMS by casting (soft lithography), resulting in holes arrays of 2-15 µm diameter and 1 µm depth. The same resist pattern can also be transferred into the under layer substrate by using reactive ion etching with a typically depth of $1 \mu m$. The residual resist could be removed by rinsing the substrate in acetone. For nanometers features, we used soft UV nanoimprint lithography as described previously [10]. After pattern transfer by gold thin film deposition and lift-off, nano-holes of diameters of 150-600 nm could be obtained over a large area.

2.2. Physical assembling method

Two techniques were investigated in this study to assembly nanoparticles in the area of lithographic patterns (Fig. 1). In the first approach (a) a small droplet $(1 \mu L)$ of polystyrene nanoparticles (800 nm diameter) solution is deposited directly on the patterned PDMS substrate. Because of the capillary force during evaporation, the polystyrene beads were assembled into the holes. In the second approach (b) a microfluidic cell in which a glass plate (with only one injection hole) was placed 10 µm above the patterned substrate without sealing. The polystyrene nanoparticles solution was injected from the hole into this cell. Once the solution has filled the void space between two substrates, the excess liquid around the injection holes was removed with a syringe. The liquid slug confined between the two substrates then moved slowly due to evaporation, and the capillary forces exerted on the edge of this liquid will push the particles across the surface of the patterned substrate until they were trapped into the patterned areas of the template.

2.3. Chemical assembling method

Now, soft UV nanoimprint lithography has been used to obtained nanometer features on a gold layer deposited on a glass substrate. The substrate was firstly treated with oxygen plasma, which can produce -OH functional group in the nano holes where the surrounding areas surfaces were protected by the gold layer. Then, we used the same surface functionalization protocol as reported previously for the immobilization of the amino group ($-NH_2$) in the holes [11]. Finally, the substrate was immersed in the solution of the polystyrene beads functionalized with -COOH and labeled with fluorescence (Fig. 2).



Fig. 1. Schematic representation of two physical assembling methods.



Fig. 2. Schematic representation of chemical assembling method.

3. Results and applications

We have demonstrated the feasibility of both physical and chemical assembling methods. Fig. 3 shows SEM images of the assembled particles in the patterned holes using the second physical method (Fig. 1b). We found that with the give pattern and particle characteristics, it is quite difficult to use the first physical approach for large area particle assembling, because there is no control of the displacement speed of the contact lines. For the second method, on the contrary, the capillary forces were sufficiently strong to push the particles into the template holes when the liquid dewetted from the bottom surface. For the same reason, almost no particle has been left on the surface of the template. If the particle concentration of the solution was high enough, each template hole would be filled with the maximum number of particles as determined by geometrical volume.

Fig. 4 shows SEM images of the nanoparticles assembled into nano-holes of the gold layer with diameter 150 nm (a), 450 nm (b) by using chemical assembling techniques. Fig. 4c shows fluorescence image of the resulted simple, which confirms the reliability of nanoparticle assembling into lithography defined small size features.

3.1. Application to nano patterning

In order to prove the applicability of the proposed method, self assembled particles have been used as template for high density pattern production. The advantage of this approach relies on the fact that the whole fabrication process is simple and low cost for the manufacturing high density pillar areas compared to the conventional techniques. Our first test consists of assembling micro polystyrene beads on the surface of a silicon wafer by evaporation. Under optical condition, particles can be assembled regularly to form a mono layer pattern. They can then be used as etch mask to transfer particle patterns into the under layer silicon substrate using reactive ion etching with SF₆ plasma. Fig. 5a shows SEM image of the remaining PS beads and the supporting silicon structures with an etch depth of 3 µm. Alternatively, pattern transfer has been tested using a PDMS template. First, polystyrene particles were assembled in the area of a patterned PDMS substrate. Then, the PDMS template was placed against a thin layer photo curable resist spin coated on a silicon substrate (particle patterns in contact with the resist layer). Finally, after UV exposure, the polystyrene particles were fixed on the top of the resist layer, which can then be used for different



Fig. 3. SEM images of the assembling polystyrene beads $(0.8 \,\mu\text{m})$ on patterned surface using a micro fluidic cell for slow evaporation and enhanced capillary force.



Fig. 4. SEM images of patterned gold surface with 150 nm diameter holes (a) and 450 nm diameter holes (b), and the fluorescence image of dye doped polystyrene beads confined in the nano holes (c).



Fig. 5. (a) SEM image of self assembled polystyrene beads (3 μ m) on silicon surface, after reactive ion etch into the silicon substrate with an etch depth of 3 μ m and (b) image of nanoparticles transferred into photo curable resist.



Fig. 6. Fluorescence images of the T4 DNA in a micro fluidic channel filled of self assembled SiO₂ nanoparticles, under an applied voltage of 30 V (a), 90 V (b) and 100 V (c).

purposes. Fig. 5b shows microphotograph of nanoparticles transferred onto the top of the resist layer. Compared to other nanofabrication techniques, using self-assembled nanoparticles as etch mask to definer nano patterns is more convenient, fast and cost effective. Further investigation has to be conducted for various applications in the field of nanophotonics, nanomagnetism as well as nanoelectronics device fabrications.

3.2. Application to single DNA molecule stretching

In recent years, microfluidic devices for bio-molecular analysis have been studied for their ability to isolate, manipulate, and investigate single bio-molecules. It has been demonstrated that DNA molecules inserted partly into a nanopillar array with an applied electric field experience a confinement-induced entropic force, causing them to recoil from the array, when the field is turned off [12]. Here, we used the assembled nanoparticles to replace nanopillars. T4-bacteriophage DNA molecules were stained with the bis-intercalating dye YOYO-1, the buffer consisted of 445 mM Tris-borate and 10 mM EDTA. Firstly, the micro fluidic channel (width: 80 µm and depth: 5 µm) was assembled with silicon dioxide nanoparticles (150 nm), the buffer solution was injected to fill the channel, a small droplet of T4 DNA solution was injected in the entry reservoir. Then, by applying an electric forces, the DNA molecules were driven into the channel and pass through the nano particles. When the applied tension is higher than 100 V, we can clearly observe that the DNA molecules can be stretched to long chain. Under low voltage condition, the DNA molecules will be relaxed and recoiled. Fig. 6 shows the fluorescence images of the T4 DNA molecules under an applied voltage 30 V (a), 85 V (b) and 100 V (c). The electric driven process of DNA from nanopatterned geometries has already proven its potential to separate DNA by length [13]. This preliminary experiment was the first step toward a low cost device manufacturing that is suited for high efficiency microfluidic separation of DNA and protein molecules.

4. Conclusion

In summary, we have demonstrated both physical and chemical techniques to assemble nanoparticles into micro and nanometer features fabricated by using optical lithography or soft UV nanoimprint lithography. The assembled particles have been transferred onto a UV curable resist layer or onto a silicon wafer using reactive ion etching. Finally, by using assembled nanoparticles into a micro fluidic channel, stretching of single-strand T4 DNA molecules has been demonstrated, thereby providing a simple approach for a high efficiency separation of DNA molecules.

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