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Patterning a Two-Dimensional Colloidal Crystal by Water-Mediated Particle Transfer Printing

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We report a new particle transfer printing (pTP) method that uses a water-mediated transfer process. Water-mediated pTP is based on the direct transfer of a two-dimensional (2-D) colloidal crystal film from a poly(dimethylsiloxane) stamp to a substrate via water-mediated surface bonding between the stamp and the substrate. In water-mediated pTP, the water layer serves as an adhesion layer to provide good conformal contact and form strong covalent bonding between the silica colloidal particle and the Si substrate. The transferred 2-D colloidal crystal patterns are chemically bound to the substrate surface and, thus, exhibit strong adhesion.

Introduction

Patterning is essential to modern science and technology. Typical applications include microelectronics,[1] microelectromechanical systems (MEMS),[2−4] biological and chemical sensors,[5−8] microfluidics,[9−12] display units, and optoelectronic devices.[13] Among existing patterning methods, soft lithography is the most efficient method to fabricate new types of structures and devices on planar, curved, or flexible substrates at a low cost.[14] Soft lithography includes a number of nonphotolithographic techniques that use a patterned elastomer (primarily poly(dimethylsiloxane) (PDMS)) as a stamp, mold, or mask to transfer the pattern to the substrates.[15] Several soft lithographic techniques, based on the process of transferring a variety of solid films (such as metals, particles, and polymers) from a stamp to a substrate, have been developed.[16−19]

Colloidal particles periodically arrayed with appropriate spacing, widely known as colloidal crystals, exhibit different colors according to their glancing angles caused by changes in the symmetry of the structure as they interact with light in space. Colloidal crystals have attracted a great deal of attention due to their potential application as sensing,[20,21] optical,[22,23] and photonic band gap materials[24,25] and for the creation of highly ordered macroporous materials,[26−28] and high-strength ceramics.[29] Usually, specific microstructures of the colloidal crystals are anticipated for their device applications, such as chemical and biochemical sensors and photonic chips. Recently, Yang et al. developed a layer-by-layer lift-up process to pattern the colloidal crystal using a PDMS stamp.[19] This method only selectively removes colloidal crystals from the substrate surface to the PDMS stamp surface using a lift-up process.

Recently, we developed a new nanotransfer printing method that is based on the transfer of a metal thin film from a stamp to a substrate via a water-mediated surface reaction.[30] In this water-mediated transfer method, the water layer serves as an adhesion layer that provides good conformal contact and forms strong covalent bonds between the metal thin film and the substrate. Here, we report a new

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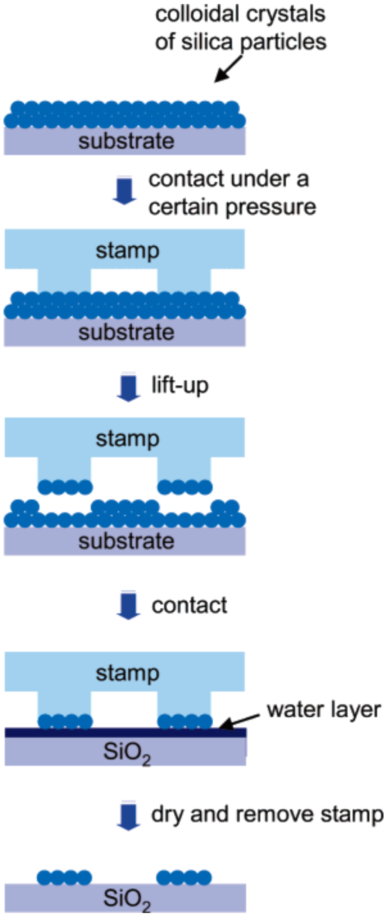

Figure 1. Schematic outline of the procedure to fabricate patterned 2-D colloidal crystal films by using water-mediated pTP.

particle transfer printing (pTP) method that uses a water-mediated transfer process. Figure 1 presents the procedures for patterning 2-D colloidal crystal films with the water-mediated pTP. This method consists of three key steps. The process begins with the preparation of uniform silica particle arrays by dropping a colloidal suspension on an inclined Si wafer. Second, a PDMS stamp with a patterned feature is brought into conformal contact with the colloid crystal films on the silicon wafer and carefully peeled. A close-packed colloidal monolayer is coated only on the raised regions of the patterned stamp. Finally, this stamp is brought into contact with a substrate coated with a water layer. After drying, the separation of the stamp leads to a patterned 2-D colloidal crystal on the substrate. This procedure can generate 2-D colloidal crystal patterns that chemically bond to the substrate surface and, thus, exhibit strong adhesion.

Experimental Procedures

Materials. Tetraethoxyorthosilicate (TEOS, 99.9%, Aldrich), ethanol (99.9%, Aldrich), and NH_4OH (28% NH_3 in water, Aldrich) were used as received. PDMS (Sylgard 184) was obtained from Dow Corning. Deionized water was purified with a Millipore Milli Q plus system, distilled over $KMnO_4$, and then passed through the Millipore Simplicity system.

Preparation of Substrates. The Si substrates used in this research were cut from *n*-type (100) wafers with resistivity values in the range of 1−5 Ω cm. The Si substrates were initially treated by a chemical cleaning process proposed by Ishizaka and Shiraki. The cleaning process consisted of degreasing, HNO_3 boiling, NH_4OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen to remove contaminants.[31] A thin oxide layer was grown by placing the Si substrate in a piranha solution (4:1 mixture of H_2SO_4/H_2O_2) for 10−15 min. The substrate was rinsed several times in deionized water (resistivity = 18 MΩ) and then dried using a stream of nitrogen.

Preparation of Colloidal Particles. The monodispersed silica particles used in this study were prepared by the Stöber process[32] using TEOS, ethanol, NH_4OH, and deionized water as starting materials. TEOS was hydrolyzed by a small amount of water in ethanol solutions with ammonia. The reagents were mixed and stirred in a water bath (Fisher isotemperature heating circulator model 2013P) at 50 °C for 50−100 min, under a N_2 atmosphere. The sol was purified by several cycles of centrifugation, decantation, and resuspension in absolute ethanol to remove undesirable particles and to prevent continuous reaction and finally dried in a vacuum oven at 100 °C. The average diameter of the silica particles prepared by this method was about 500 nm.

Preparation of Stamps. Masters were fabricated by using conventional photolithography to pattern resists on silicon wafers. The masters had parallel lines and spaces with dimensions from 10 to 3 μm. PDMS stamps were produced according to a previously reported procedure.[14−16] The stamps were fabricated by casting PDMS on the masters. After curing, the PDMS stamps were peeled away from the masters. When the stamps were made using these masters, the raised lines of the master corresponded to the recessed spaces of the stamps.

Analysis Techniques. Measurements of the mean size and size distribution of the prepared SiO_2 colloidal particles were conducted by a light scattering system (Microtrac UPA-150). Secondary electron microscopy images were obtained using a JEOL JEM-3010 instrument. Conventional Scotch-tape adhesion tests, which are simple and reliable, were performed to qualitatively assess the adhesion performance of the colloidal crystal patterns to the Si substrate. In this test, the adhesion tape was simply applied to the sample surface and subsequently peeled off. If the adhesion is good, the tape peels off cleanly, and if adhesion is poor, part of the structure is removed with the tape.

Results and Discussion

Preparation of 3-D Colloidal Crystals. Monodisperse silica particles (500 nm in diameter) were redispersed in ethanol in a vial. A piece (10 cm × 10 cm) of silicon wafer was vertically submerged in the silica solution and then dried in an environmental chamber (RH = 74% and 45 °C) for approximately 2 h. The colloidal particles were crystallized into a close-packed structure several layers thick on a silicon wafer, as shown in Figure 2. The thickness of the colloidal crystal films was adjusted by controlling the silica content (typically 0.07−0.21 wt %).

Formation of a Single Layer of Close-Packed Particles on a PDMS Stamp. A PDMS stamp with patterned features was brought into conformal contact with the colloidal crystal film surface on the silicon wafer under a certain pressure. After the PDMS stamp was carefully peeled away, a single layer of the colloidal crystal film was transferred to the protruding surface of the PDMS stamp. Figure 3 shows the

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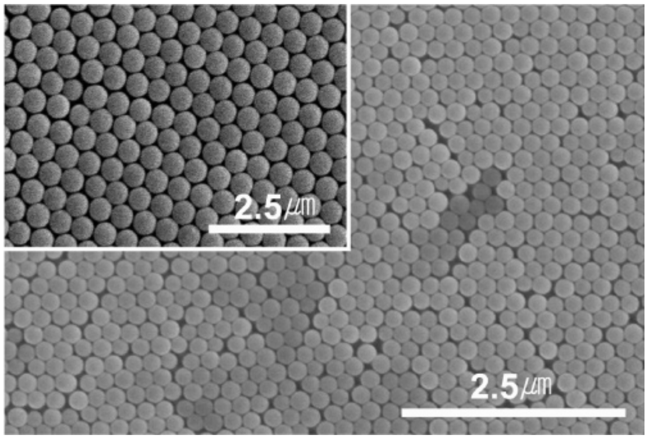

Figure 2. SEM images of 3-D silica colloidal crystal films on the silicon wafer.

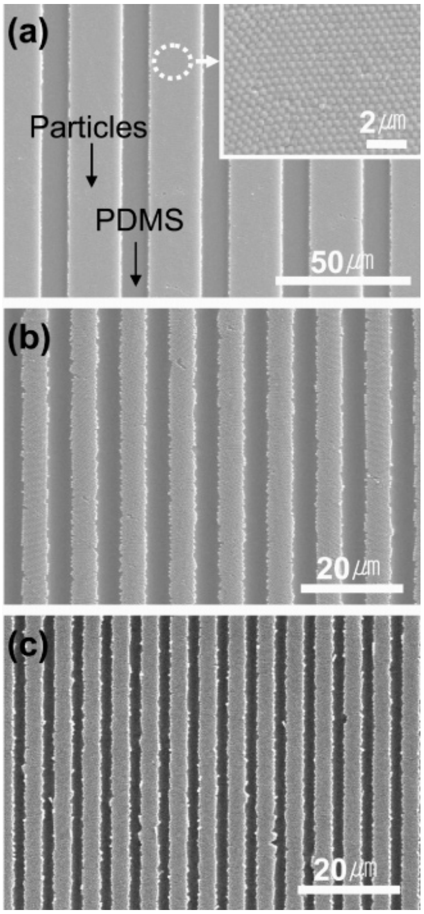

Figure 3. SEM images (a−c) of the protruding surfaces of the PDMS stamps peeled from the 3-D colloidal crystal films on the silicon wafer.

surfaces of the PDMS stamps peeled from the colloidal crystal films using the lift-up process. A layer of hexagonally arrayed colloidal particles could be clearly observed only on the protruding surfaces of the PDMS stamps fabricated by using the masters having 10.2, 4.9, and 2.5 μm parallel lines with 19.8, 5.1, and 3.5 μm spaces, respectively. These results demonstrate that the interaction between the PDMS stamp surface and the silica colloidal particles is greater than that between the silica particles and the silicon wafer.

Formation of Patterned 2-D Colloidal Crystals on Si Substrate. The PDMS stamp coated with a layer of hexagonally arrayed colloidal particles was brought into contact with the oxidized Si substrate with a water layer. We found that the thickness of the water layer was not critical to the transfer of the colloidal particles, provided that the layer covered the whole surface of the substrate. The Si substrate (1 cm × 1 cm) can be uniformly covered with a 100 μm thick water layer by using 10 μL of water. The stamp, in contact with the substrate, was dried at room temperature. After drying, the separation of the stamp led to a patterned close-packed array of colloidal particles on the substrate. The RH was kept at 40% in all experiments. Figure 4 a−c shows the SEM images of the 2-D colloidal crystal patterns fabricated by using the PDMS stamps having 19.8, 5.1, and 3.5 μm parallel lines with 10.2, 4.9, and 2.5 μm spaces, respectively. These images clearly show that the colloidal crystal patterns retain the dimensions of PDMS without noticeable line spreading.

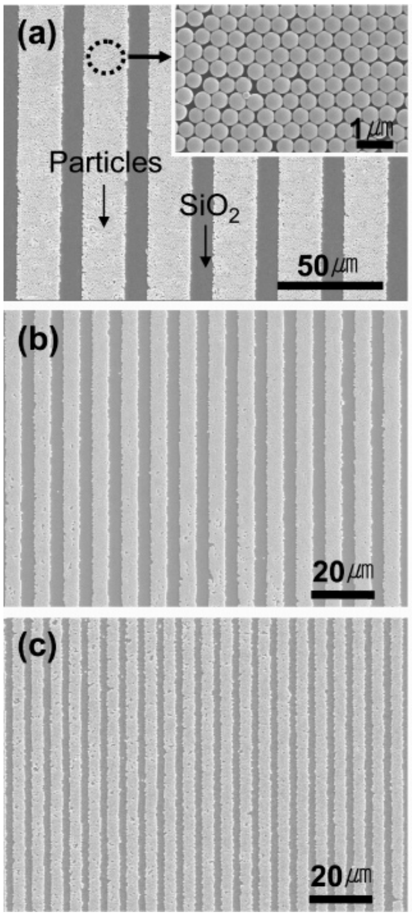

Figure 4. SEM images (a−c) of patterned 2-D colloidal crystal films fabricated on the Si substrates by using water-mediated pTP.

In this water-mediated pTP method, the water layer on the substrate is the most critical part and serves as an adhesion layer to promote the adhesive bonding between the colloidal particles and the substrate. The water-mediated pTP can be explained by two different types of bridges formed by the water layer. One is a liquid bridge, or a so-called capillary bridge, which contributes to good conformal contact between the stamp and the substrate. The silica particles on the stamp have a high surface energy due to hydroxyl groups, where the water contact angle is about 10°. A thin oxide layer was grown on the Si substrate by chemical oxidation with a piranha solution. Such hydrophilic surfaces exhibit strong capillary action as they come into contact with a thin water layer. As the water evaporates, the attractive capillary force gradually increases to pull the two surfaces into contact and provides good conformal contact between them with no additional pressure to the stamp. In the drying process, the adhesive strength between the silica particle and the Si substrate is significantly strengthened by the formation of covalent bonds between the two surfaces, similar to the process of wafer bonding. This last phenomenon has been termed as solid bonds or bridges and is observed in cases when the microstructures are left to dry following the final water rinse.[33−39] Materials from the silica particle and Si surfaces dissolve into the water layer and reprecipitate between the two surfaces during the drying process, thereby producing the strong solid bonds. The capillary bridge provides good conformal contact, and the solid bridge forms strong covalent bonding between the colloidal crystal film and the Si substrate. The water-mediated transfer process results in the permanent attachment of the colloidal crystal patterns to the Si substrate at the regions of contact. The transferred colloidal crystal patterns easily passed the Scotch tape adhesion tests.

Conclusion

We described a new pTP method based on the transfer of a 2-D colloidal crystal film from a stamp to a substrate via a water-mediated surface reaction to form chemical bonds between the colloidal crystal film and the substrate. In this water-mediated pTP, the water layer serves as an adhesion layer to provide good conformal contact and form strong covalent bonding between the 2-D colloidal crystal and the Si substrate. The water-mediated pTP method was applied to the preparation of 2-D colloidal crystal patterns with various feature sizes on Si substrates.

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