Fabrication of Highly Resolution Colloidal Crystal Array on Patterned Substrates by Ink-Jet Printing

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Abstract

Self-assembled colloidal patterns have been fabricated on a substrate using inkjet printing with an ink of submicron-sized monodisperse silica particles. The ink are prepared with well-dispersed suspension of monodisperse silica particles. Dot patterns are formed on both hydrophilic silicon wafer and hydrophobic silicon wafer modified with octadecyltrichlorosilane. It was found that the uniformity and spatial extent of the self-assembly within a dot were significantly influenced by the interaction of the ink with substrates and its drying behavior. For the improvement of pattern resolution, we treat a silicon wafer with OTS by a contact-printing. Chemically heterogeneous substrate has repeated stripe patterns of hydrophilic and hydrophobic properties with different relative widths. When jetting conditions are well controlled, we demonstrate to directly print the line pattern with the width of 21 μm, which is difficult to achieve by the conventional ink-jet printing. The internal and external structures of the colloidal aggregates were observed by scanning electron microscope (SEM) and confocal microscopy.

Introduction

Self-assembling ability of monodisperse colloidal spheres into crystalline arrays makes them interesting and versatile building block for advanced materials. Highly ordered structures of colloids exhibit a number of potentially usable characteristics such as light diffraction and photonic band gaps,[1] high surface-to-volume ratio, and enhanced catalytic reactivity.[2] The formation and utilization of such colloidal assemblies have been an intriguing subject of research over the past several decades. One of the self-assembling methods involves the use of a "droplet of colloidal suspension" as a template.[3] Uniform liquid droplets containing a number of colloidal particles can be generated in the form of water-in-oil emulsion using a droplet break-off technique. As the suspending solvent is slowly removed from the droplet, the crystallization of colloids occurs inside the droplet, forming spherical colloidal aggregates of controlled sizes. These aggregates may serve as precursors for more complex colloidal assemblies. In this communication, we have compared the deposition patterns of the colloid when the colloidal inks ejected from a drop-on-demand ink-jet nozzle are placed on various substrates.

Ink-jet printing is an emerging technology, being explored extensively beyond image transfer capability, with many applications including microdispensing and materials assembly. Recently it has been used to fabricate polymeric electro-luminescent,[4] controlled release drug delivery devices in pharmaceuticals,[5] and refractive microlenses made of hybrid organic-inorganic materials.[6] A major challenge in applying ink-jet processes for directly writing materials is formulating suitable inks. Ink chemistry and formulations not only dictate the quality of the printed image, but they also determine the drop ejection characteristics and the reliability of the printing system.[7]

Furthermore additional functionality can be augmented by endowing the ink with self-assembling properties. Fan et al. demonstrated to fabricate hierarchically organized nanostructures by ink-jet printing.[8] Their approach involves the use of molecular-scale, self-assembling surfactant as an ink component. Selective deposition of such a functional ink by ink-jet printing forms macroscopically patterned nanostructures as similar to printing visual information onto paper. We further elaborate the procedure by using mesoscale, self-assembling colloidal ink consisted of monodisperse silica microspheres. Nearly uniform sized ink droplets are rapidly produced to selectively place on arbitrary surfaces by ink-jet printing. Silica particles contained in each ink droplet undergo self-assembly on evaporation, producing colloidal aggregates with internal ordered structure. Varying interfacial properties of the surfaces with which the ink interacts can control the size, shape, and self assembled structures of the colloidal aggregates. We further demonstrated to improve the line resolution of the ink-jet printing using a chemically heterogeneous substrate. Controlling the relative widths of the hydrophilic/hydrophobic stripes produces a very fine line deposit of the colloids.

Experimental

Monodisperse silica (σ=700nm) was purchased from Bangs laboratory Inc. Formamide (Aldrich Chemical Co.), n-octyl alcohol (Aldrich Chemical Co.), and deionized water were added to make the colloidal dispersion containing 2~4% silica by volume. The colloidal ink was printed by an ink-jet printer onto various substrates. The printer set up consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured from Microfab Technologies, Inc. (Plano, TX) with a 30-μm orifice. P-type Si wafer of [100] orientation was used as a hydrophilic substrate. Silicon wafer was modified with a self-assembled monolayer (SAM) of octadecyl-trichlorosilane (OTS) to produce a hydrophobic surface (OTS-SAM/Si). Furthermore, micro-contact printing of OTS produced a series of chemically patterned substrates of a different feature of the hydrophilic/hydrophobic periodic properties. Relative widths of the hydrophilic/ hydrophobic stripes were varied. The pattern morphology and microstructure of the resulting colloidal crystals were investigated by confocal microscopy and scanning electron microscopy.

Result and Discussion

The microstructures of the primitive dot generated by a single droplet ~ 70 pL of the colloidal ink were shown in Fig. 1. Macroscopic shape and dimension of the dots differs from the substrate type and ink concentration. Evaporation of liquid droplets containing microspheres placed on the hydrophilic Si formed ring-shaped deposition of the monolayered silica when the ink concentration was below 4 vol%. With increasing particle concentration, the width of the ring becomes thicker, and at 4 vol% the complete circular deposit of the diameter ~ 130 μm was obtained. Further increase in the concentration produced the spherical deposit with multilayered colloids. In contrast, hemispherical colloidal assemblies of smaller diameter ~ 26 μm were fabricated on the hydrophobic OTS-SAM/Si. It was also observed that self-assembled structures and its spatial extent of colloidal silica inside the dot were significantly influenced by the substrate types. On the Si wafer, a relatively well ordered 2D colloidal monolayer was observed at the periphery of the ring, whereas a cluster of the monolayered colloids was randomly scattered inside the ring. On the other hand, on the OTS-SAM/Si, the silica microspheres were arranged in a three-dimensional long-range ordered structure. The resulting hemispherical colloidal aggregates had very smooth surface, displaying large domains of hexagonally packed particles as well as a few point and line defects. Packing factor of silica within the colloidal aggregate was much higher than other surfaces, reflecting higher structural ordering.

Different configuration of the colloidal deposition patterns reflects varying wettability of the ink depending upon the substrate types. The ink droplet experiences distinctively different shrinkage motions depending on its configuration.[9] The ink droplet of a low contact angle printed on the silicon wafer forms a very thin liquid layer at the three-phase contact line where the solid/liquid/gas interfaces meet. Thus the peripheral of the droplet dries much faster than its center, upon which the suspending particles consolidate there. This prevents the contact line of the evaporating droplet recede (i.e., pinning), so the droplet must change the shape from cap-like to disk-like with a fixed base diameter as it decreases in volume. The suspension together with the suspending silica at the center is drawn to the drying front to replenish the liquid removed from the edge and eventually is depleted. The consolidated colloidal assembly grows radially by addition of the incoming particles. Such a drying behavior of the droplet force the colloidal silica randomly arranged in a center of the ring-shaped particle deposition. The ink droplet placed on the OTS-SAM/Si, on the other hand, retains a hemispherical shape (neglecting gravitational effect) with a high contact angle. The presence of thicker liquid layer at the contact line of the droplet permits uniform slow evaporation to occur throughout the liquid/gas interface. In such a case, the contact line is not pinned rather than retracts as the droplet shrinks while maintaining a hemispherical shape. The silica particles suspended in the evaporating droplet are gradually concentrated as the solvent slowly evaporates. When the particles concentration reaches a certain critical value at which their mobility is significantly reduced with the decrease in droplet volume, the particles start to crystallize in close vicinity to the external surface, and the incoming particles become crystallized when they contact the ordered arrays of the particles, growing colloidal crystal.

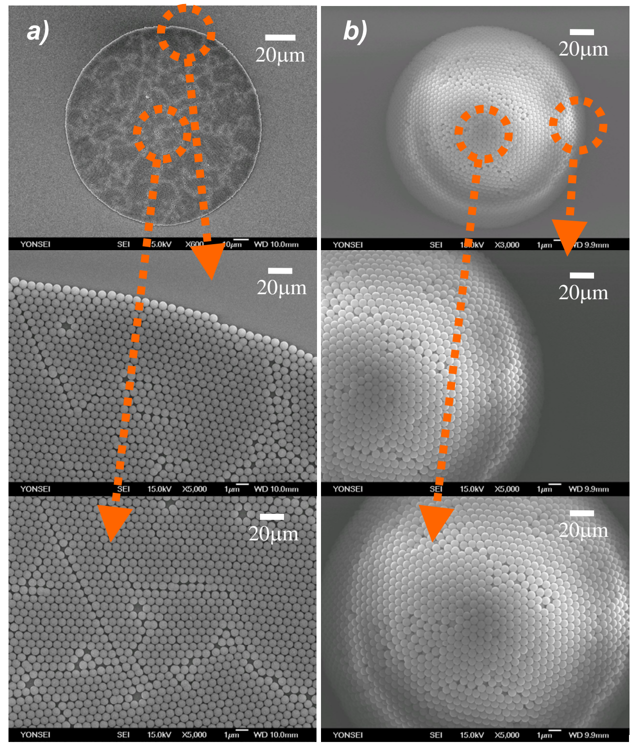

Figure 1. SEM images of the deposition patterns composed of the silica microspheres produced by ink-jet printing a single ink droplet on two different substrates: (a) silicon wafer and (b) OTS-SAM film.

Narrowing the single dot-to-dot distance makes individual dots merged. When the inter-dot distance becomes less than the diameter of the single dot, the continuous lines form. At the dot-to-dot distance ~ 150 μm, the continuous line with a undulated finish was observed as shown in Fig. 2(a). The particle distribution within the line pattern was uneven in which most of the particles were deposited in a monolayer near the line border whereas few particles were scattered in the center. This result indicates that the pinning also occurs at the triple phase boundary during line printing. At the dot-to-dot distance ~ 100 μm, the line pattern with a smoother finish was produced. Interestingly, the particles were uniformly distributed, forming the high quality line-shaped colloidal crystals of well-packed monolayer (Fig. 2(b)). Ink droplets placed in a proper separation distance merge to form a line-shaped colloidal liquid deposit that contains the appropriate numbers of the particles filling up completely its occupied area during the drying. This result clearly demonstrates the capability to directly write the 2D photonic crystal pattern using an ink-jet printing. On the other hand, because of high contact angle, the formation of line pattern on the OTS-SAM/Si was difficult to achieve. Each droplets placed on the surface were moved to merge together, forming a separated larger droplet as shown in Fig. 2(c).

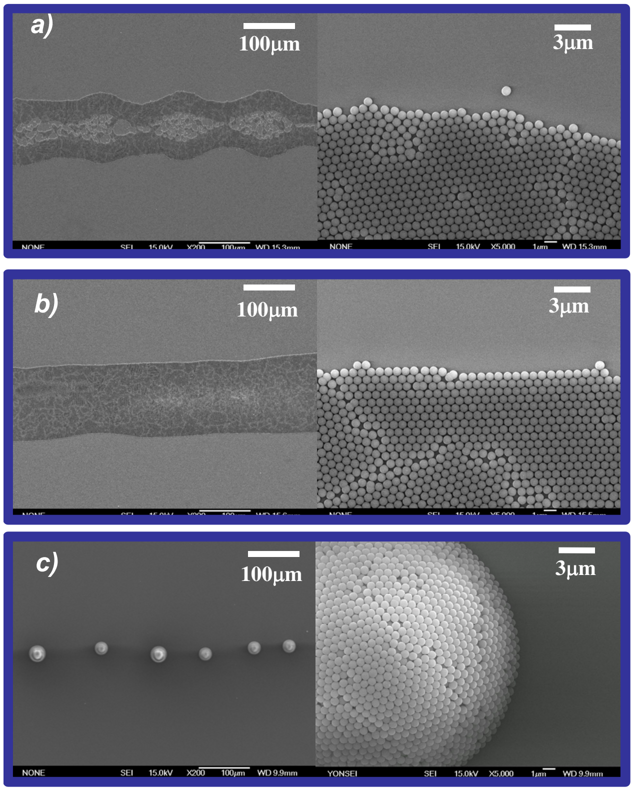

Figure 2. SEM images of the line patterns composed of the silica microspheres produced by ink-jet printing a multi ink droplet on two different substrates: (a), (b) silicon wafer and (c) OTS-SAM/Si.

In the case of printing on the hydrophilic substrate, the ink wets well the surface and spreads significantly. The ink droplet of ~53 µm in diameter prior to impact resulted in the dot pattern of ~ 130 µm. The width of the line patterns became further broaden, reaching to ~ 140 µm. This poor resolution is an inherent drawback associated with the ink-jet printing. In our study, we have tried to ink-jet printing the colloidal ink onto the chemically heterogeneous patterned substrate to improve the resolution limit. For liquid features in the micron range, the surface to volume ratio is exceedingly large. Thus, the energetics associated with the boundary surface and interfaces determine the overall shape and stability of liquid microstructures. If we use deliberately tailored physicochemically heterogeneous substrates, it is possible to control the morphological pathways of dewetting and the morphology of resulting colloidal deposited structures with much improved resolution.

Figure 3 shows the deposit patterns produced by ink-jet printing a single ink droplet on the chemically patterned substrates with different hydrophilic stripes. The width of the microstructure varied from 14 µm to 35 µm. As a printing condition, the diameter of ink droplet was ~53 µm prior to impact, traveling at a velocity of 2.9 m/s. Each droplet was aimed to place on the center of the hydrophilic region. The macroscopic morphology of the deposit pattern varied with the chemically patterned substrates. When the drop radius is of the same order as the hydrophilic stripe width, the ink droplet deposited on substrate became distorted from its spherical shape. The ink droplet placed on the hydrophilic stripe with the width of 35 µm resulted in a distorted spherical deposit since the contact line of the ink was almost circular with only small deviations near the stripe boundaries.[10]

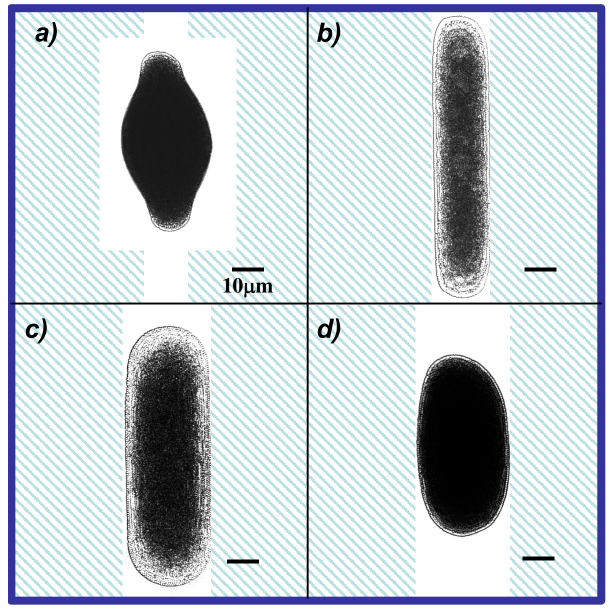

Figure 3. Confocal microscopic images of the deposit patterns composed of the silica produced by ink-jet printing a single droplet on chemically heterogeneous pattered substrates: the hydrophilic line widths differ from (a) 14µm, (b) 21µm, (c) 28µm and (d) 35µm. The shaded region represents the hydrophobic surface.

Due to less occupied area by the ink droplet, the particles are rather accumulated as a thick deposit after drying. The deposit pattern width was defined by that of the hydrophilic stripes. As the hydrophilic width became narrow, the deposit pattern changed into a highly elongated shape with narrower width as shown in Fig. 3(b). The deposit pattern also became thinner. At the stripe width of 21 µm, we have a line shaped deposit with the same width defined by the hydrophilic stripe. However, further reducing the hydrophilic width was unable to make the ink droplet spontaneously dewet from the hydrophobic region. The resulting deposit rather maintained spherical morphology with two bulged parts due to partial wetting on the hydrophilic region (Fig. 3(a)) [12].

The behavior of a droplet residing on the chemically heterogeneous surface is somewhat complicated. However, its understanding would provide us a useful and practical route to achieve very fine line resolution far below the limit of the conventional ink-jet printing. If jetting condition (that means ink property, jetting speed, etc) is well controlled, the final line quality could be controlled by the relative widths of the hydrophilic/hydrophobic stripes.

Conclusions

We have controlled the morphology of particle assemblies from hemispherical structure to pellet-shaped dot pattern with ordered internal structures by ink-jet printing the colloidal ink. The ordered colloidal structure was generated by evaporating the solvent of the ink, which induces monodisperse silica microspheres self-assembled within a droplet template. We have also investigated the behavior of a micron-scale droplet impinged on chemically heterogeneous patterned substrates. When the drop radius is of the same order as the hydrophilic stripe width, the final droplet shape becomes elongated, forming a fine line pattern beyond the resolution limit inherent to conventional ink-jet printing. Our process described here is very simple, it can be anticipated to enable us rapidly producing functional, hierarchically organized structures in arbitrary designs, which may be of practical importance for directly writing fluidic and photonic devices, along with displays and sensor arrays.

Acknowledgements

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