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High resolution patterning of nanoparticles by evaporative self-assembly enabled by *in situ* creation and mechanical lift-off of a polymer template

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High-resolution patterning of nanostructured materials into open templates is limited by the processes of creation and removal of the necessary template. In this work, a process for forming a micropatterned template from cellulose acetate polymer *in situ* on the substrate is demonstrated. Nanoparticles are patterned by evaporative self-assembly, and the template is removed by mechanical means. The process is demonstrated by patterning zinc oxide nanoparticles on silicon and cyclic olefin copolymer substrates and by creating a highly sensitive ultraviolet light detector. © *2011 American Institute of Physics*. [doi:10.1063/1.3671084]

Open template nanoparticle patterning processes, such as screen printing or lift-off processes, are attractive due to their simplicity and versatility, allowing a wide variety of materials to be patterned in their natural form without chemical modification.[1–3] Unlike inkjet or electrohydrodynamic printing, the process is not dependent on the solvent or nanoparticle concentration of the ink and allows for a much higher patterning throughput.[4,5] Compared to other template-based patterning methods such as micromolding in capillaries (MIMIC)[6] or microfluidic molding,[7] there is more flexibility in the patternable geometries, enabling more than just continuous features. However, the resolution of screen printing is currently limited to the features of 100 μm or larger due to the inability to create a suitable template with the proper feature size and a sufficiently intimate contact between the screen and the substrate.[8] Additionally, the versatility of lift-off processes is limited by the chemical dissolution of the template, which requires the removal of the template and excess nanoparticles without damage to patterned features or redeposition of nanoparticles on the substrate.[3] In the presented work, a micropatterned template is created from cellulose acetate polymer *in situ* on the substrate. This template is shown to have adhesion to the substrate that is sufficient for proper deposition of the nanoparticles by natural evaporation of a sessile droplet, yet weak enough for efficient removal by mechanical lift-off.

The patterning process is illustrated schematically in Figure 1. A polymer template with low adhesion to the substrate is first created by microfluidic molding of the polymer dissolved in solvent, followed by coffee-ring effect-based deposition of nanoparticles into the template.[7] Briefly, clean solvent (acetone) is patterned on a substrate by pressing with a vapor-permeable, patterned poly(dimethylsiloxane) (PDMS) mold. The mold is held in contact with the substrate using a light pressure not exceeding 7 kPa. Cellulose acetate polymer dissolved in acetone is introduced to the outside of the mold. As the solvent evaporates and diffuses through the vapor-permeable mold, the polymer ink is drawn into the mold and concentrated. When the solvent is fully evaporated, the mold is removed, leaving the polymer template. Following template creation, a brief oxygen plasma is used to ensure that the water film spreads on the substrate, preventing non-uniform deposition of nanoparticles caused by the Marangoni effect. At this point, a droplet of nanoparticles in solvent (zinc oxide nanoparticles in water) is placed on the surface of the polymer template and allowed to evaporate at room temperature. A convective transport of the particles induces the formation of coffee-ring deposits, and the nanoparticles fill into the patterned features uniformly assisted by the induced corner flow[3] and the enhanced electrostatic attraction between the particles and the substrate due to deprotonation of the substrate resulting from the oxygen plasma treatment.[9] When the system is dry, an adhesive tape is adhered to the surface of the polymer template. The tape is then pulled from the surface, removing the polymer template and trapping any residual particles between the template and the tape, preventing them from settling on the substrate.

Zinc oxide nanoparticle patterns on silicon and cyclic olefin copolymer (COC) substrates are shown in Figure 2. A large, dense array of isolated squares of particles with a width of 20 μm at a 1:1, 1:2, and 1:4 spacing was formed on the substrate. Each individual square showed good, uniform packing of nanoparticles with no visible cracks or defects. The heights of the patterned features were found to be quite uniform over the printed area, except for an increase in feature heights near the location of the coffee ring on the template and were controllable by varying the concentration of the nanoparticle ink. It is interesting to note that the pinning of the contact line by nanoparticles at the edge of the droplet plays a significant role in ensuring uniform deposition of nanoparticles inside the coffee-ring region. While nanoparticles are being deposited downward by an electrostatic attractive force induced by the hydrophilic surface charge, excessive particles are convectively transported toward the edge and form a thick coffee-ring deposit. This transport is caused by a hydrodynamic effect of an evaporating droplet and occurs only if the contact line is pinned at the edge of the droplet.[3,10] If the volume fraction of the particles is too low, the contact line will not be pinned and particles will be

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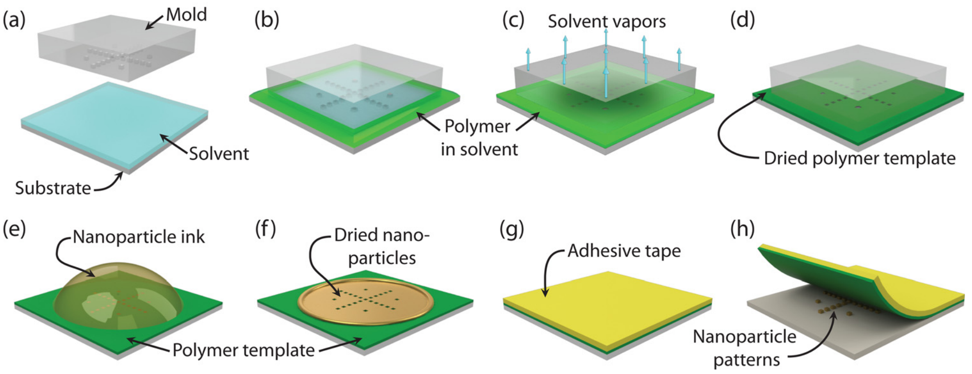

FIG. 1. (Color online) The patterning process. (a) A vapor permeable polymer mold is positioned above a substrate coated with clean solvent. (b) The mold is used to pattern the solvent, and polymer ink is introduced around the sides of the mold. (c) The solvent evaporates and diffuses through the mold, drawing the ink inside and concentrating the polymer, until (d) all of the solvent is removed and only polymer remains. (e) The mold is removed and a droplet of nanoparticle ink is placed on the polymer template. (f) The nanoparticle ink solvent dries, leaving a coffee-ring. (g) Tape is placed over the template and coffee ring, and (h) the template is pulled from the substrate, leaving only the nanoparticle patterns.

deposited as it recedes, causing variation in the feature heights. The thinnest features to be uniformly deposited were created using a 1 wt. % nanoparticle solution, resulting in a layer with a thickness around 300 nm and with dimple structures caused by an instability at the particle suspension-air interface.[11] Finally, the sidewalls of the patterned features do show some fracture due to a shearing force caused by the mechanical lift-off, resulting in nearly 45° sidewalls, which are seen to be very repeatable.

To further characterize the lift-off process, the peeling forces required to remove the cellulose acetate from the silicon or COC substrates and the tape from the cellulose acetate were measured. Details of the measurements are given in the supporting information.[12] The peeling force required to remove the cellulose acetate from silicon was 3.8 ± 0.5 kN/m and from the COC was 2.1 ± 0.3 kN/m. The force to remove the tape from the cellulose acetate was 100 ± 10 kN/m. The difference in peeling force of over 25 times explains the reliability with which the mechanical lift-off can be used to remove the template without leaving any residual template on the substrate. That is, a strong adhesion between the template and the tape is used to overcome a weak adhesion between the template and the substrate, allowing complete and simple removal of the template.

Finally, to demonstrate a practical application of nanoparticle patterning using this method, an ultraviolet (UV) light detector was created by patterning a 400 μm^2 square of zinc oxide nanoparticles between two gold electrodes on a silicon dioxide substrate. An optical micrograph of the fabricated sensor and the response of the sensor to various wavelengths of UV light are shown in Figure 3. A cellulose

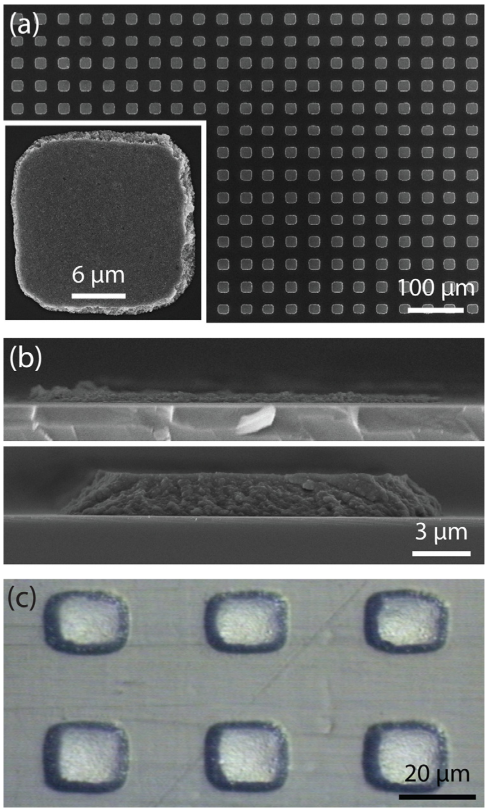

FIG. 2. (Color online) SEM micrographs of (a) ZnO nanoparticles on a silicon substrate in a large array with 1:1 spacing and individually (inset), and (b) the height of patterns using 1% (above) and 2% (below) concentration inks. (c) Optical micrograph of ZnO nanoparticles on a COC substrate.

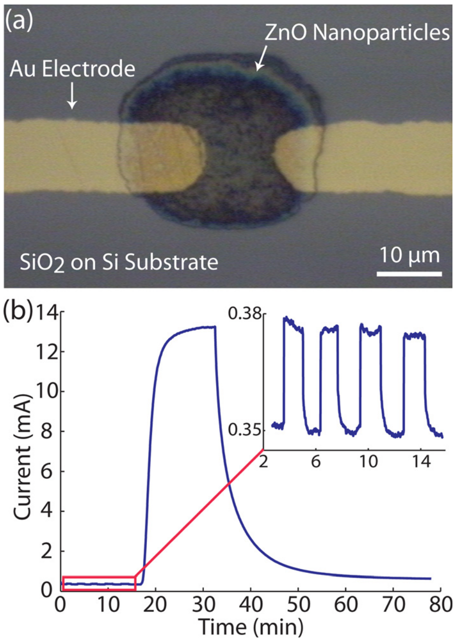

FIG. 3. (Color online) (a) An optical micrograph of the fabricated UV light sensor. (b) The current response of the sensor under a constant bias of 20 V when flashing 365 nm light (0-16 min) and 254 nm light (after 18 min) at an intensity of 71 mW/cm^2.

acetate template was patterned on the electrodes by the method described above, using a specially designed alignment system. Once the cellulose acetate pattern was made, the zinc oxide nanoparticles were deposited and lift-off was completed as described earlier. Further details of the sensor and a more complete characterization of the sensor performance are given in the supporting information.[12] The sensor compares favorably with existing zinc oxide nanoparticle UV light sensors, having a sensitivity of 9.707×10^4 A/W. However, unlike previous zinc oxide nanoparticle sensors, the fabrication process is greatly simplified, allowing the formation of nanoparticle patterns without requiring chemical ligands, surfactants, stabilizers, or any solution-based removal processes which may chemically modify the particles and adversely affect the final performance of the fabricated device.

A simple and versatile process for patterning nanoparticles was characterized by patterning zinc oxide on two different substrates. The results show that accurate and repeatable patterning is possible in this very simple and scalable method. The patterning was further demonstrated by creating a UV light sensor by aligning zinc oxide nanoparticle patterns on gold electrodes. The general nature of the patterning method and its non-specificity to the materials and solvents involved makes it interesting for use in many other types of applications where patterns are to be formed with different nanoparticle or substrate combinations without chemical modification of the ink or chemical perturbation of the nanoparticles.

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[12] See supplementary material at http://dx.doi.org/10.1063/1.3671084 for further information about materials, experimental procedures, and device characterization.