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Integration of Metallic Nanostructures in Fluidic Channels for Fluorescence and Raman Enhancement by Nanoimprint Lithography and Lift-off on Compositional Resist Stack

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Abstract

We present and demonstrate a novel fabrication method to integrate metallic nanostructures into fluidic systems, using nanoimprint lithography and lift-off on a compositional resist stack, which consists of multi-layers of SiO_2 and polymer patterned from different fabrication steps. The lift-off of the stack allows the final nano-features precisely aligned in the proper locations inside fluidic channels. The method provides high-throughput low-cost patterning and compatibility with various fluidic channel designs, and will be useful for fluorescence and Raman scattering enhancement in nano-fluidic systems.

Keywords

Nanoimprint lithography; compositional resist stack; aligned patterning; fluidic channel; metallic nanostructures; fluorescence and Raman scattering

1. Introduction

Metallic nanostructures have been widely used in sensing applications, such as surface-enhanced Raman scattering (SERS) [1, 2], bio-molecule sensing [3–5], and enhanced fluorescence imaging [6–8]. The integration of such metallic nanostructures into fluidic systems is very desirable to sensitive and fast molecular detection. Previously, photolithography [9] and electron beam lithography (EBL) have been used to make nanostructured optical sensors [10,11], mechanical sensors [12], and chemical sensors [13] in fluidic systems. Nanoimprint lithography (NIL) [14, 15] provides an alternative fast and large-area patterning approach to build nanostructures in fluidics for bio-molecular detection [16–20]. Here we present a novel NIL-based method to integrate metallic nanostructures into fluidic channels. Different from the previous work, our approach can be applied not only to semiconductor and dielectric materials but also metallic materials. Furthermore our approach is simple yet very effective: using NIL and selective patterning, it simultaneously allows fast patterning of various nano-structures and reliable sealing of the fluidic channels, providing opportunities for bio-sensing applications integrating nano-fluidics and nano-optics.

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2. Device structure and fabrication by “Lift-off using compositional-resist stack (LUCS)”

The device we fabricated consists of micro-fluidic channels of different widths (2–8 μm) with nanoscale metal array inside the channel (Fig. 1). The entire fabrication has three segments: (i) patterning micro-fluidic channels in fused silica substrate, (ii) patterning the nanoscale metal structures, and (iii) sealing the top of the microchannel using a slide.

To precisely align the metal nanostructure array inside the microchannels, we have developed a novel process, termed “lift-off using compositional-resist stack (LUCS)”, where the resists layers accumulated from several lithography steps in the fabrication form a 3D stack, which has all information regarding the size, area and alignment of nano-features. Therefore, when the metal nanostructures are lifted off by removing the resist stack, they are not only well-defined over a large area, but also accurately defined by the dimensions of the stacks and precisely aligned into the designed regions inside microchannels.

The major fabrication steps are: (1) pattern micro-fluidic channels in fused silica substrate using SiO_2/ARC as the mask (Fig. 1 a–c), (2) without removing the remaining first SiO_2/ARC layer, spin-coat a second layer of SiO_2/ARC, and pattern the SiO_2 into a strip (Fig. 1 d–f), (3) spin-coat a third resist and imprint nanoholes in the resist, (4) transfer the nano-holes all the way to the fused silica through a Cr nano-mask (Fig. 1 g–h), (5) deposit and liftoff metal using the multilayer resist stack as the template to form the metal dots only in the desired locations in the microchannel (Fig. 1 i), (6) optionally etch the nanopillars in fused silica followed by other processing, and (7) seal the top with a glass plate.

Here the LUCS used a compositional mask of three resist stacks: the first two stacks each consist of SiO_2 and ARC (a crosslinked polymer similar to anti-reflection coating material [21], XHRiC-16 from Brewer Science, Inc.), and the third layer is the top imprint resist.

To fabricate the microchannels bearing SiO_2/ARC stack, 1” square fused silica wafers were thoroughly cleaned by solvents (acetone and 2-propanol) and RCA-1 (NH_4OH:H_2O_2:DI water = 1:1:5, 80°C, 15 min), and then deposited with bottom-stack SiO_2/ARC (10/30 nm thick, ARC baked at 180°C for 30 min). Photolithography (resist AZ 5214E, ~1.4 μm thick) and reactive ion etching (RIE, Plasma Therm SLR 720) were then used to pattern SiO_2/ARC/fused silica, etching through the SiO_2/ARC stack and forming 50 nm deep channels in fused silica substrate. CHF_3 (10 sccm, 150 W, 5 mtorr), oxygen (10 sccm O_2, 50 W, 2 mtorr), and CF_4/H_2 (33/7 sccm, 300W, 50 mtorr) were used in RIE for SiO_2, ARC, and fused silica, respectively. The photoresist was then solvent-stripped (Fig. 1c).

The middle-stack SiO_2/ARC (15/40 nm thick) layers were then deposited on the patterned fused silica wafers, and defined into rectangular openings crossing the fluidic channels by a second photolithography and RIE (Fig. 1 d–e). The photoresist was then removed, exposing the selective nano-pattering windows in the middle SiO_2/ARC stack (Fig. 1f). In this way, only the fluidic channel regions overlapped with the lithography-defined openings, where both the SiO_2/ARC stacks were etched away, would be patterned with nano-features.

To create uniform nano-features in NIL, the fused silica substrate was planarized with thermal imprint resist (Nanonex NXR-1025, 250 nm) by a flat Si mold (200 psi, 130°C, 5 min) in a nanoimprinter (Nanonex NX 2000) (Fig. 1g). The flattened resist was imprinted to form 200 nm pitch nanohole arrays (200 psi, 130°C, 4 min), and then covered with 5 nm thick Cr nano-hole mask by shadow-evaporation [22, 23] (Fig. 1h). Finally, the resist residual layer was removed by O_2 RIE, and Au/Cr nano-dots of 30/3 nm thick were nano-patterned in the channels (Fig. 1i) by e-beam evaporation and lift-off in RCA-1 (80 °C, 10

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min). The fabricated device can then be treated with ozone and sealed with a clean fused silica coverslip.

3. Results and discussions

In our test, we fabricated micro-channels of various widths (2–8 μm) (Fig. 2a), and patterned the nano-feature windows to 10 μm and 20 μm wide, as shown from the optical image (Fig. 2b). The nano-feature windows were not aligned to the channels lithographically but simply designed to cross them, only relying on our LUCS approach to achieve desired self-alignment. The bottom SiO_2/ARC stack was laterally aligned during micro-channel RIE process to the edges of fluidic channels, hence patterning the nano-dots only in channels within an error of a few nanometers. This method allows a large alignment tolerance and greatly reduces the fabrication complexity.

The planarization step before NIL was found critical to eliminate defects (Fig. 3). Using the same imprint resist (~250 nm thick) and the same processing parameters, NIL on a non-planarized substrate caused a large number of defects (Fig. 3a), while it yielded uniform nano-patterns on the planarized substrate (Fig. 3b). The poor resist filling on the non-flat fused silica was due to the large surface roughness, which was ~150 nm from fluidic channels to the stacked SiO_2/ARC layers (atomic force micrograph (AFM) image Fig. 3c). In comparison, the planarization reduced the surface roughness to 2 nm (Fig. 3d), and thus allowed a much more uniform imprint over a large area (Fig. 3b and 3e).

In NIL, a 200 nm-pitch nano-pillar mold of 15×15 mm^2 was used, with a pillar width of 60 nm and a height of 130 nm scanning electron micrograph (SEM) images (Fig. 4a–b). Imprinted nano-holes were defined in the resist uniformly, covering the different micro-patterned regions over the whole wafer (Fig. 4 c–d). As shown from the cross-sectional SEM image (Fig. 4e), the imprint resist filled faithfully inside the channels.

The liftoff of the compositional resist stack was carried out carefully in RCA1 solution, which dissolves the ARC layers and removes all the deposited metal dots on the top. After liftoff, 60 nm sized Au/Cr nano-dots of 30/3 nm thick were fabricated only in the fluidic channels (Fig. 5). The thickness of the metal nano-dots was chosen smaller than the channel depth, hence guaranteeing the full inclusion of the nanostructures inside fluidics and providing a flat surface of the fluidic device for successful device bonding and reliable testing. The nano-dots were self-aligned in channels with different widths (Fig. 5c) and further integrated into a fluidic system by patterning inlet and outlet in another photolithography and RIE (Fig. 5d). This demonstration shows our approach can provide fast and large-area nano-patterning inside fluidics, flexible integration of nano-structures to fluidic systems of various geometries, and a large tolerance in nano-scale multi-level alignment.

This LUCS approach can also be utilized to pattern non-metallic materials and/or fabricate other complicated nano-patterns, e.g. meshes, bars, and tri-angles, by simply using the corresponding imprint molds. For example, 115 nm diameter square fused silica nano-pillars were patterned by NIL using a different pillar mold and aligned in fluidic channels (Fig. 6). Using the LUCS approach, functional and more complex nanostructures, such as plasmonic disk-coupled dots-on-pillar antenna array (D2PA) [2], can also be fabricated in fluidic systems and used for real-time fluorescence and surface enhanced Raman scattering (SERS) enhancement measurements.

Through the multi-level lithography steps and self-aligned integration, the proposed LUCS nano-patterning technique allows independent control of the geometries of the micro-channels (e.g. location, width, and depth) and the nano-dots (e.g. pitch, size, shape,

thickness, and material), and thus enables the optimized flexible integration of nano-features into micro-fluidic systems. Because all the fabrication steps are standard techniques, tens or even hundreds of devices can be produced in a single batch, thus maximizing the throughput. Currently, the fabrication of a whole batch may take up to about 24 hours, mainly limited by the vacuum waiting time for evaporation. It is believed the fabrication time can be shortened by further optimization.

4. Conclusions

We present here a new method of integrating NIL-based fast nano-patterning techniques to micro/nano-fluidic systems by "lift-off using compositional-resist stack (LUCS)", and demonstrate the precise patterning of nano-dots into selected regions of fluidic channels. This method is free from complicated optical alignment and capable of patterning nano-features of different materials (e.g. metals and dielectrics) and different geometries, thus potentially enabling various fast and real-time biochemical sensing applications, such as DNA sequencing [17], molecules sorting [24], fluorescence [7], and SERS [25]. Besides, the LUCS approach can also be applied to other fields to selectively define nano-structures on various substrates, such as nano-texturing light emitting diode [26], solar cell [27], etc.

Acknowledgments

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- nanoimprint lithography patterning
- non-flat substrates
- self-aligned nano-structures
- integration with fluidic systems

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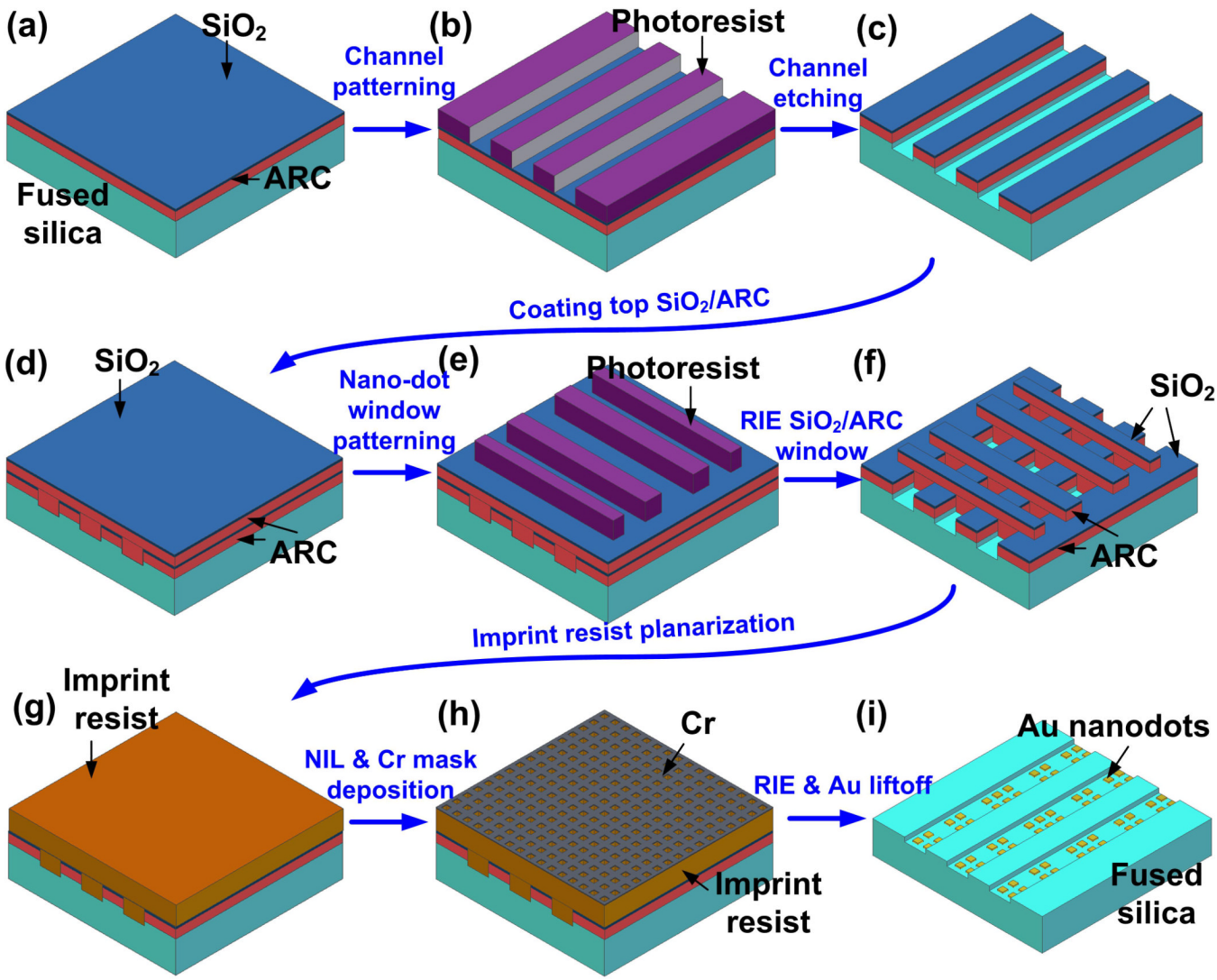

Fig. 1. Schematics of NIL patterning of Au nano-dots in fluidic channels

(**a**) Fused silica substrate coated with bottom stack of SiO_2/ARC; (**b**) Micro-fluidic channels defined by photolithography; (**c**) Micro-channels patterned in bottom SiO_2/ARC layers and fused silica, with photoresist stripped; (**d**) Middle stack of SiO_2/ARC coated on the substrate; (**e**) Second photolithography to define the nano-feature patterning window for Au nano-dots; (**f**) Nanofeature patterning window transferred to middle stack SiO_2/ARC by RIE; (**g**) Imprint resist coated and planarized on the substrate; (**h**) Nano-holes patterned in imprint resist by a nano-pillar mold and covered with a Cr mask. (**i**) Au nano-dots patterned in fluidic channels by evaporation and liftoff.

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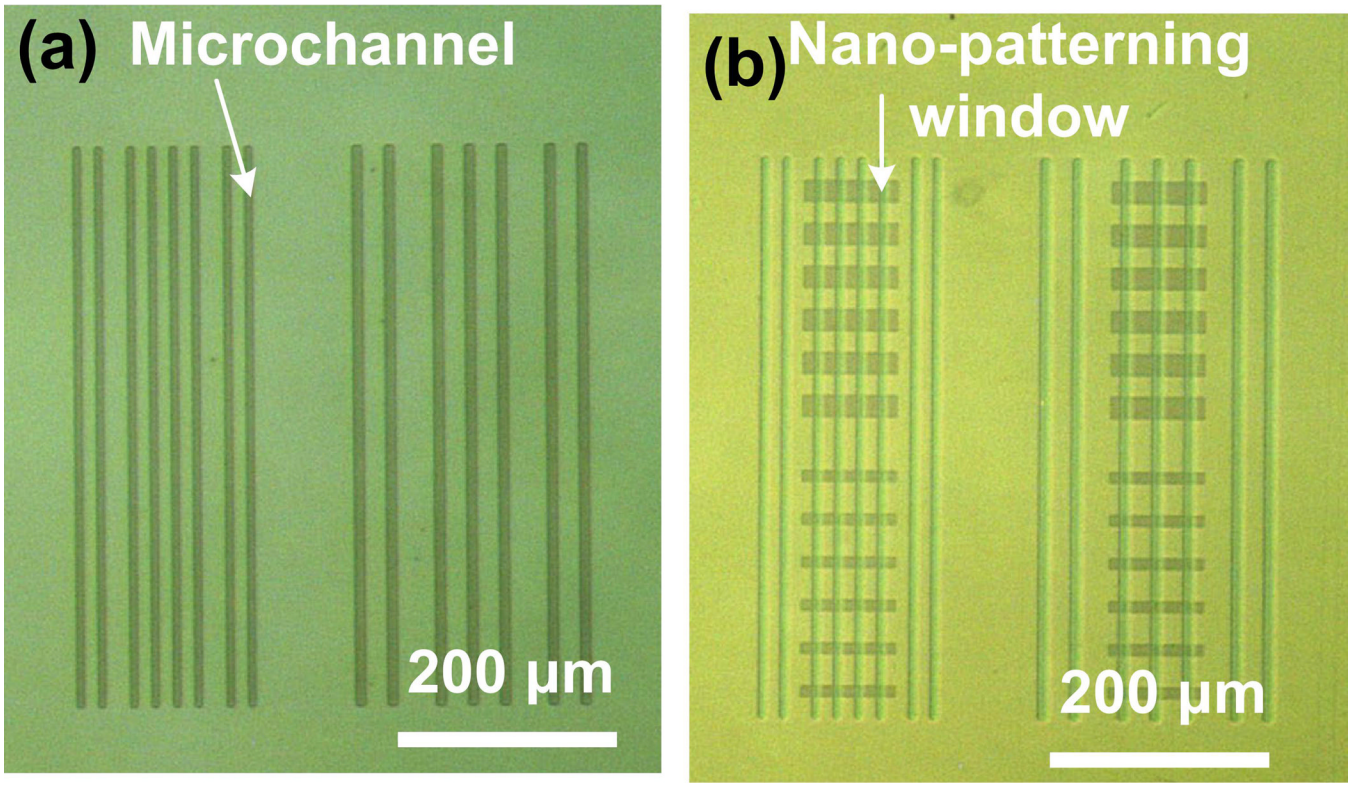

Fig. 2. Optical images of fabricated micro-channels and nano-feature patterning windows

(**a**) Micro-channels fabricated in bottom SiO_2/ARC stack and fused silica. (**b**) Nano-feature windows in middle SiO_2/ARC stack.

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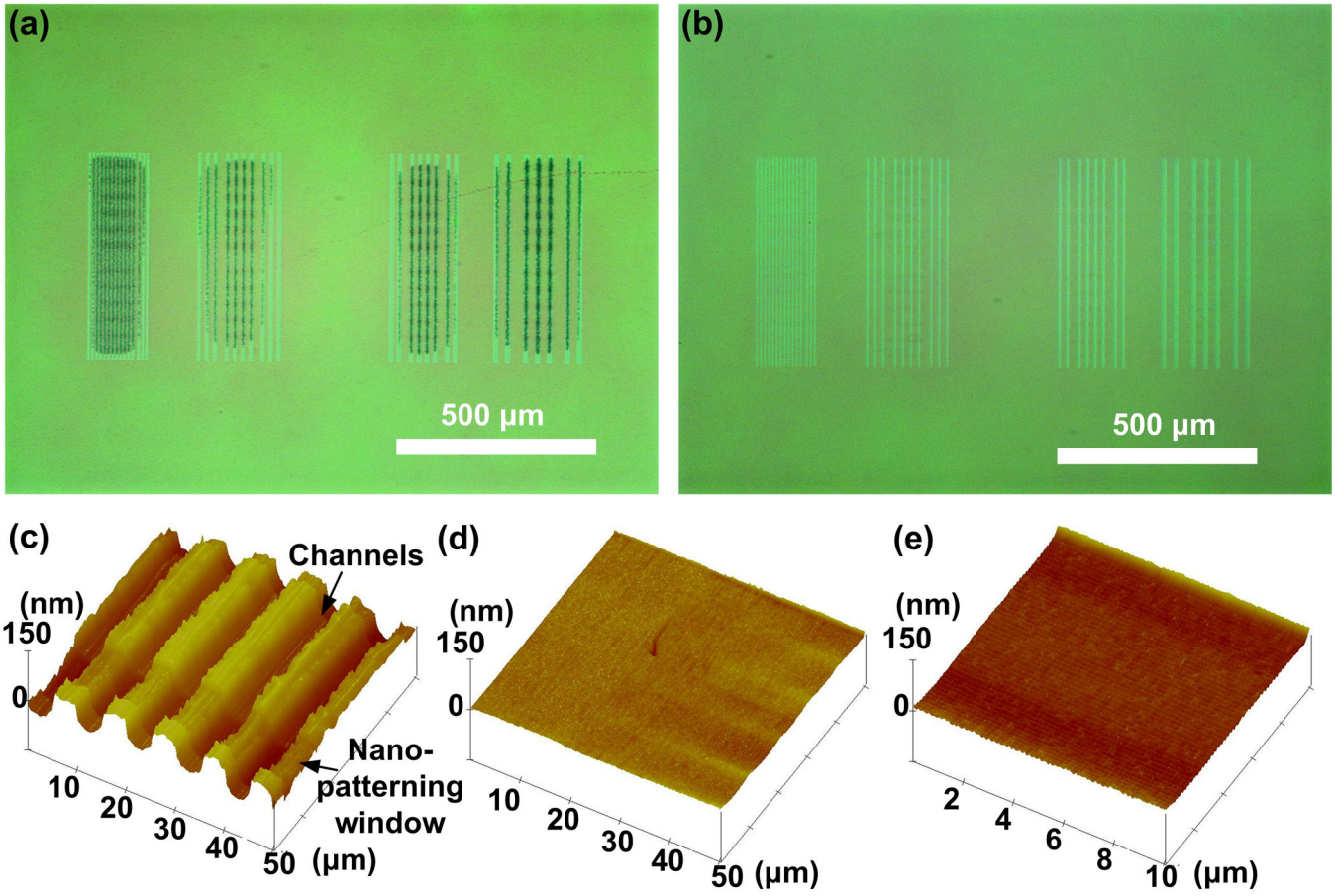

Fig. 3. Planarization and nanoimprint on non-flat substrate patterned with fluidic channels

a–b, Optical images of imprinted patterns on: (**a**) non-planarized substrate, and (**b**) planarized substrate. **c–e,** AFM images showing the surface morphologies of: (**c**) patterned substrate with SiO_2/ARC stacks; (**d**) planarized substrate with imprint resist, and (**e**) nano-holes imprinted on planarized substrate.

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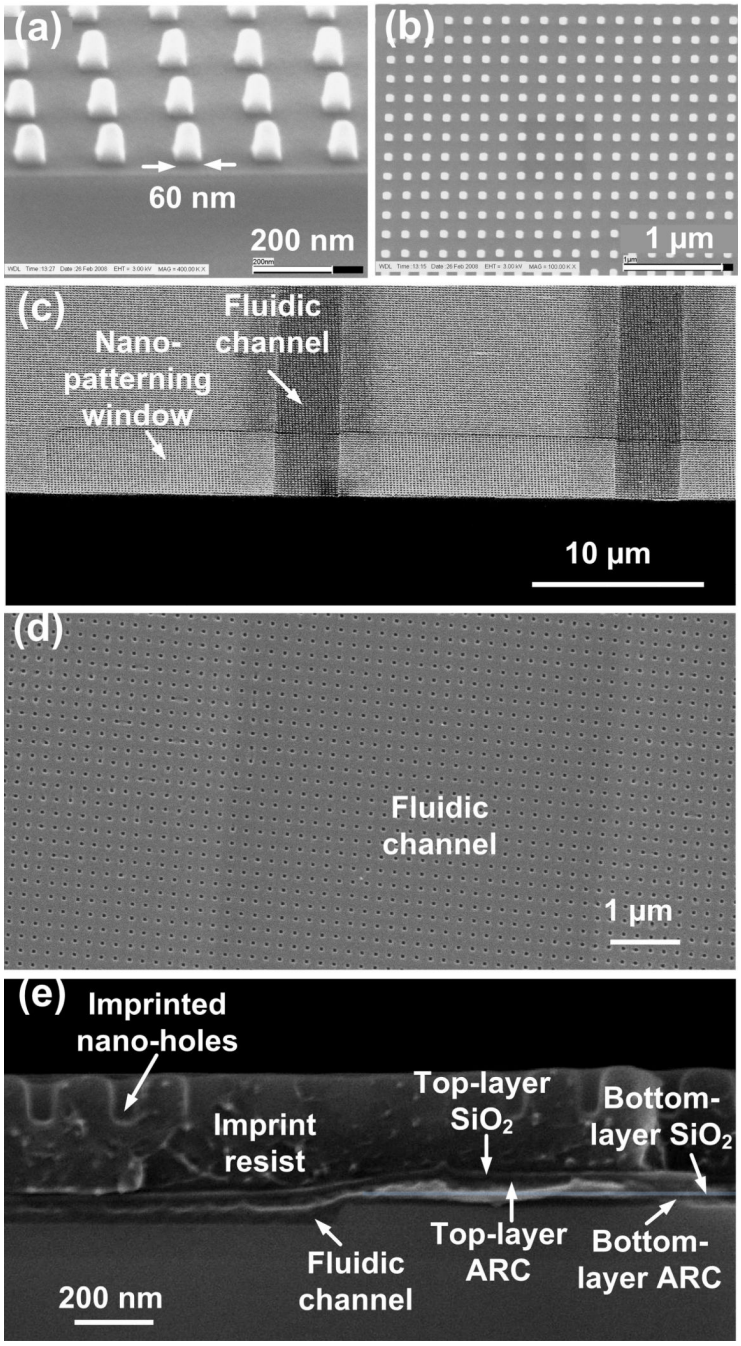

Fig. 4. Imprint on fluidic channel substrate with a nano-pillar mold

a–b, SEM images of a mold with 60 nm wide nano-pillars: (**a**) 45° side view, and (**b**) top view. **c–e,** SEM images of imprinted patterns in resist on fused silica micro-channel substrate: (**c**) 45° side view to show the micro-channels and nano-feature patterning window, (**d**) top view to show the nano-holes, and (**e**) Cross-sectional view to show the resist, SiO_2/ARC stacks, and fluidic channel in fused silica, with a light blue light indicating the thin bottom SiO_2 layer.

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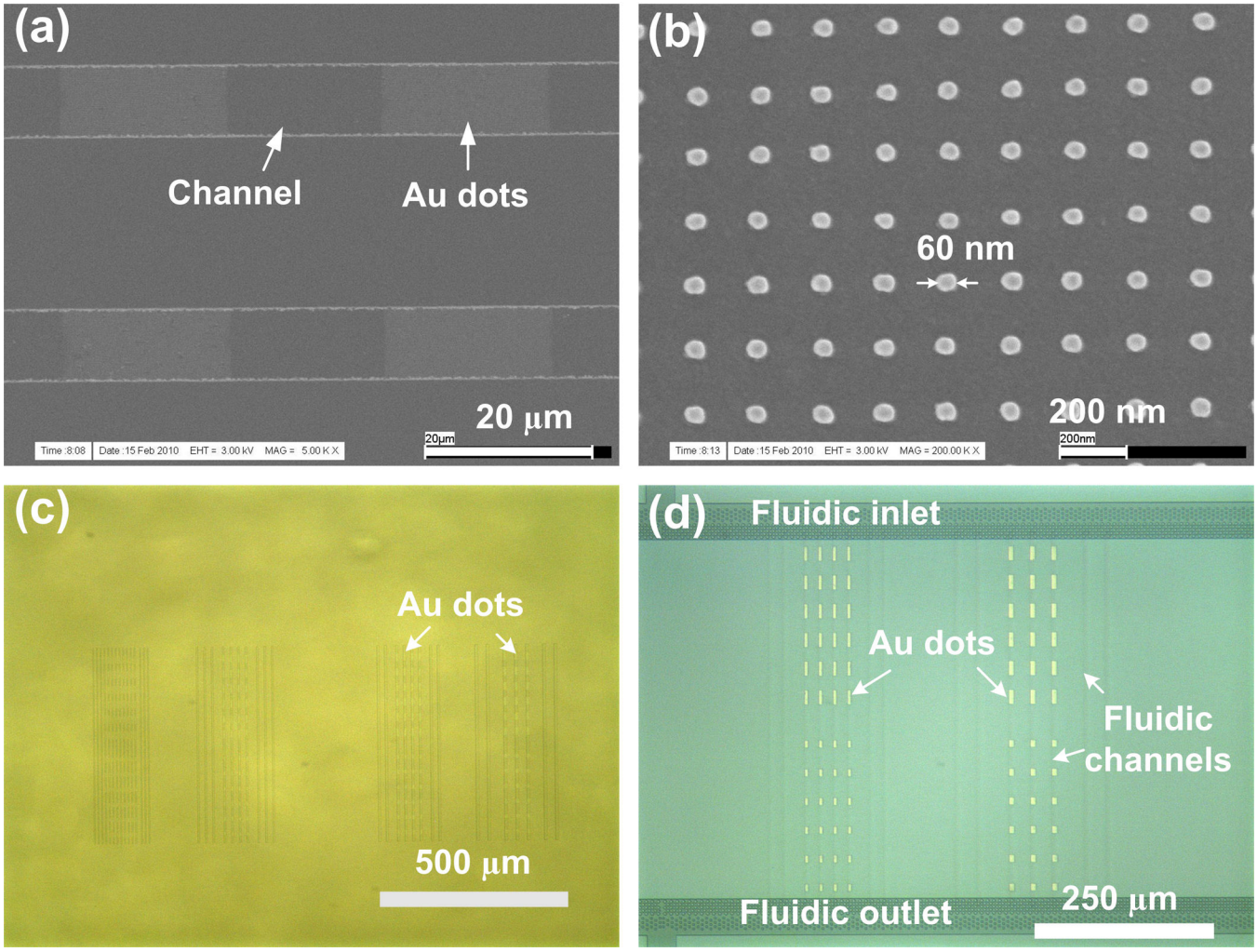

Fig. 5. Fabricated 60 nm diameter Au nano-dots aligned in fluidic channels

a–**b**, SEM images, (**c**) optical image of Au nano-dots after liftoff, and (**d**) optical image of Au nano-dots integrated in a fluidic device.

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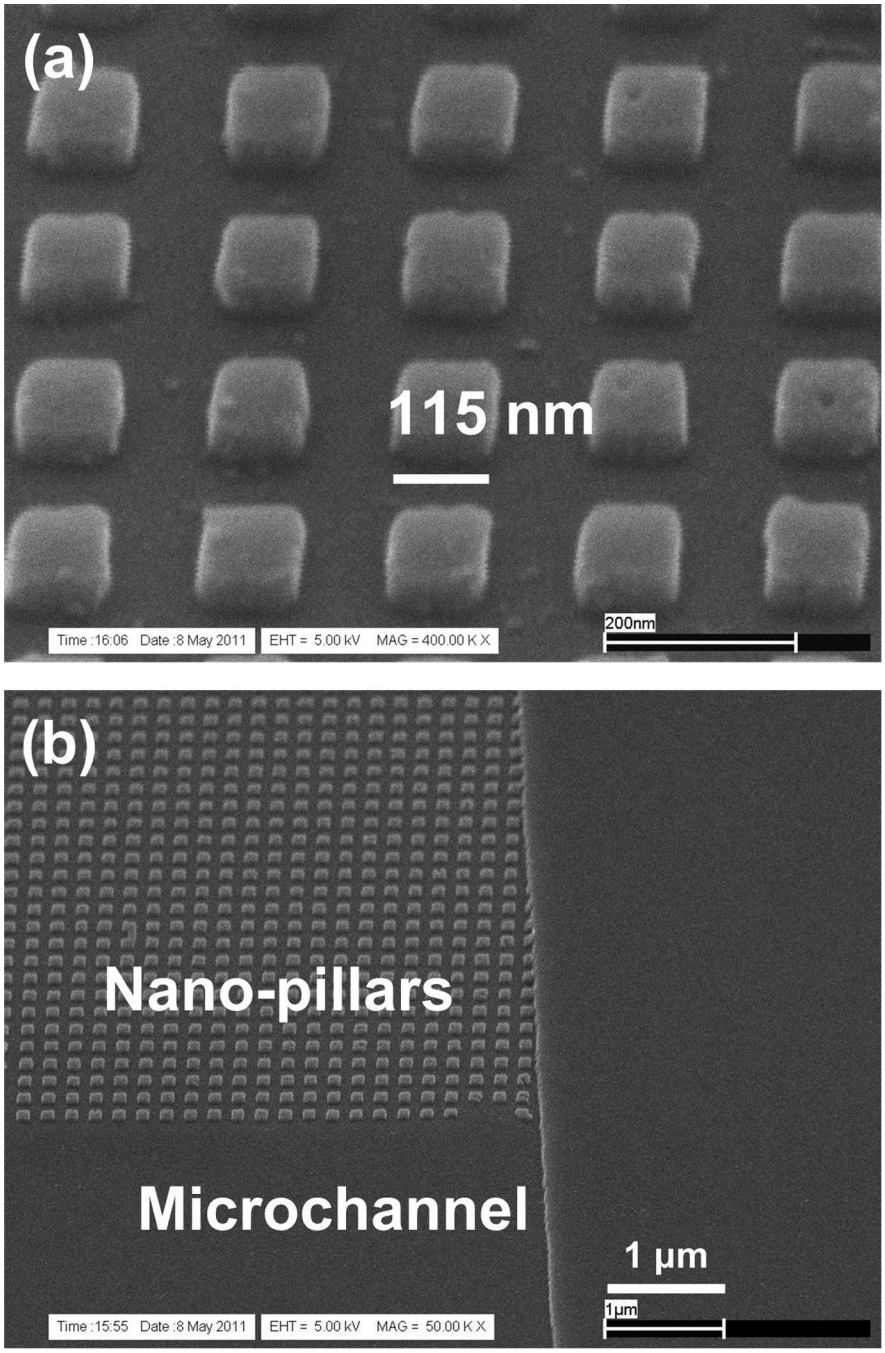

Fig. 6. SEM images of precisely aligned 115 nm wide fused silica nano-pillars in fluidic channels
(**a**) high-magnification image of rectangular nano-pillars, and (**b**) nano-pillar regions selectively patterned in channels and aligned to the channel edge.