Fast three-dimensional nanostructure fabrication by laser-assisted nanotransfer printing

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The authors present a laser-assisted nanotransfer printing technique for transferring metal nanopatterns onto prepatterned substrates. A fused quartz mold covered with an array of chromium nanodots is pressed against the surface of a photolithographically patterned substrate, while a single laser pulse from a quadrupled-frequency solid state Nd:YAG laser is used to melt the thin metal structures. By controlling the laser fluence, selective metal pattern transfer can be realized only on the protruded area of the substrate upon separation of the quartz support. The transferred chromium nanodots are then used as an etch mask to pattern three-dimensional structures. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2347693]

Three-dimensional structures having nanoscale features are commonly fabricated by multiple lithography steps [typically involving photolithography and/or e-beam lithography (EBL)] with alignment or by a single lithography step with multilayer resist stacks. However, besides the low throughput of EBL, performing lithography over topography generated by the previous patterning steps presents many challenges. Among these, the resist thickness may not be uniform across a prepatterned substrate, making critical dimension control difficult, or the coverage of resist may not be conformal with voids near the edge of the previous pattern, which impedes subsequent pattern transfer by etching.

In this letter, we describe a simple laser-based process for fast printing of metal nanofeatures over prepatterned substrates, named laser-assisted nanotransfer printing (LA-nTP). The transferred metal nanofeatures are then used as an etch mask to pattern three-dimensional (3D) structures. LA-nTP is a dry-contact printing process which combines into one single step several steps needed for metal nanopatterning, such as lithography [EBL or nanoimprint lithography (NIL)], metal deposition, and lift-off processes. This process shares some attributes with laser-induced forward transfer (LIFT) process.[1] In LIFT, a thin laser-light absorbing film is irradiated with a focused laser pulse through a transparent support, and transferred, in the form of micron-sized dots, onto a suitable substrate facing it. The pattern is created through selective deposition on the substrate by scanning the laser beam. The resolution is hence determined and limited by the laser beam size and by the gap between the two samples (which determines the lateral spreading). In the LA-nTP process, we use a prepatterned transparent support in close contact with a substrate; therefore the resolution is no longer limited by the processing parameters but is determined only by the initial feature size on the transparent support.

A schematic sequence of LA-nTP leading to the fabrication of 3D nanoscale features is shown in Fig. 1. The first step is the generation on a substrate (transparent to the laser irradiation) of the metal nanopattern to be transferred. In our case, a square chromium nanodot array [$\sim 80 \times 80$ nm^2, 200 nm period, and 35 nm thick (see inset A in Fig. 1)] was fabricated on an UV-grade fused quartz substrate using double NIL at orthogonal angle and lift-off. In parallel, we defined, by photolithography and reactive ion etching, the desired pattern into a 500 nm thick thermal SiO_2 layer. Here, for the proof of concept, we have arbitrarily chosen an array of microwells with a diameter of 100 μm, 40 nm deep, and separated from each other by 100 μm (edge to edge). The two patterned surfaces were then brought into close contact by sandwiching them between two press plates. The top plate

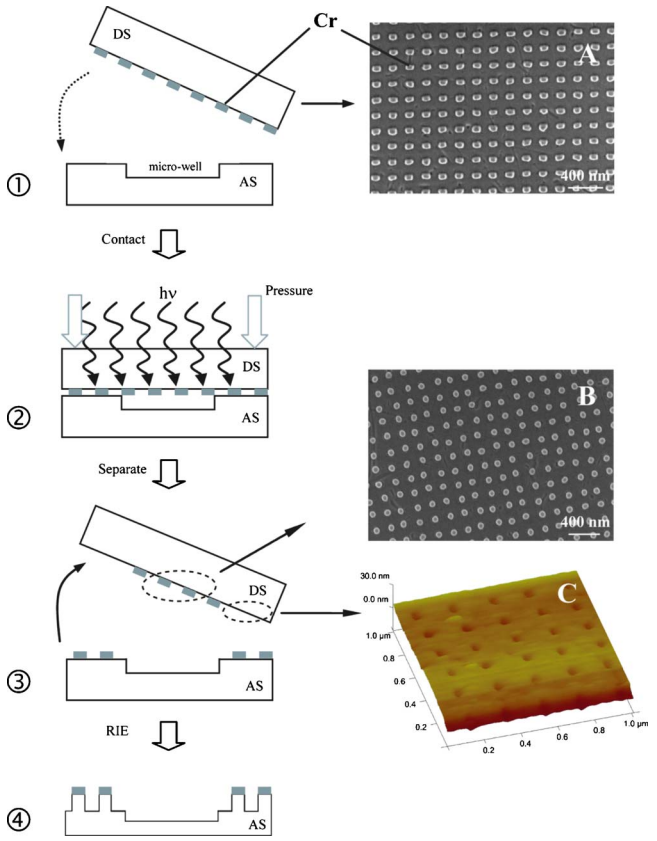

FIG. 1. (Color online) Schematic sequence of the fabrication process of 3D nanostructures by LA-nTP (DS: donor support, AS: acceptor substrate). The inset pictures show the Cr nanodot pattern on the DS before (inset A) and after (inset B) LA-nTP. The inset C is an AFM image of the quartz support after LA-nTP.

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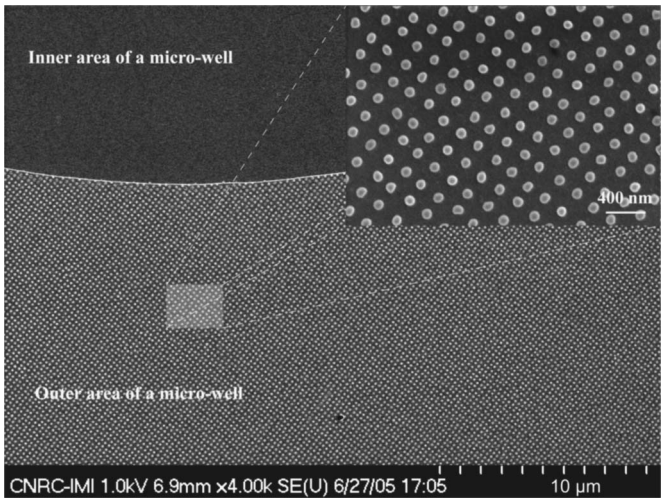

FIG. 2. Scanning electron microscope (SEM) image of the surface coverage of Cr nanodots around a microwell after LA-nTP. The inset is a zoom in of the transferred Cr nanodots on the acceptor surface.

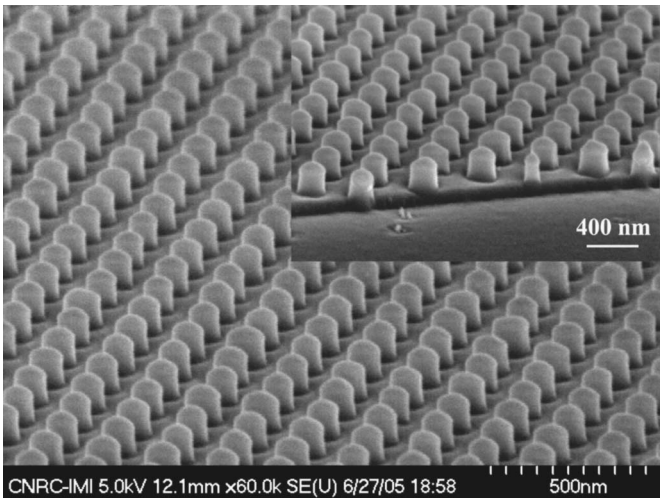

FIG. 3. SEM image of SiO_2 100 nm high nanopillars on the raised regions on the acceptor surface using the transferred Cr nanodots as an etch mask (note the remaining Cr on top of the pillars). The inset is a zoom in view of the edge of a microwell (40 nm deep).

has an opening to let the laser beam through. The silicon wafer (the acceptor substrate) was placed on the lower plate with the quartz donor support on top of it. Pressure was provided by a set of springs and was estimated from the constant of the springs to be about 0.69 MPa. The transfer printing process was realized when a single pulse from a quadrupled-frequency neodymium-doped yttrium aluminum garnet laser ($\lambda = 266$ nm) impinged the quartz support with the chromium nanopattern from the back side. The incident Gaussian laser pulse was spatially shaped using a 5 mm diaphragm and focused to a diameter of 1 mm. At a typical laser fluence of 350 mJ/cm^2, the Cr nanodots are transferred only onto the protruded parts of the acceptor substrate that are in intimate contact with the donor support.

Figure 2 shows the result of the transferred nanopattern after LA-nTP. It can be seen that the transfer follows the topography of the prepatterned acceptor substrate with an excellent control over a large scale. The protruding area around the microwell was totally covered with Cr nanodots, while none was found on the recessed area (which is only 40 nm deep). A close look at the transferred nanodots (inset of Fig. 2) and the ones remaining on the donor support (inset B of Fig. 1) reveals that LA-nTP heats Cr nanodots into a molten state, changing the initially square Cr dots into rounded dot ones due to the very high metal surface tension. The transferred and the nontransferred nanodots have a mean diameter of 95 and 80 nm, respectively, both with the same periodicity as the original pattern. This slight increase ($\sim 20\%$) of the transferred nanodots diameter during the printing transfer can be explained by the applied pressure that squeezed the melted Cr. Atomic force microscope (AFM) measurements also reveal that the height of the transferred nanodots is ~ 45 nm. The difference with the initial thickness of the Cr nanodots (~ 35 nm) might be due to the transfer of some melted silica on top of the Cr nanodots. Indeed, as illustrated in inset C of Fig. 1, we can clearly see in this AFM image the presence of tiny holes (5–10 nm deep) on the surface of the quartz plate after LA-nTP, with the same periodicity as the Cr nanodot array that was on the surface before. [It is worth mentioning that direct irradiation of the bare SiO_2 substrate at the same fluence did not lead to any melting damage due to the much larger optical penetration depth of SiO_2 ($\alpha^{-1} > 1$ cm at 0.25 μm).[2] It was also verified that the formation of these holes is not due to the fabrication process of the Cr nanodots array.] We also found that using higher fluences (>600 mJ/cm^2), the results obtained were similar to those observed in other LIFT studies,[1] i.e., Cr material was transferred on the protruded areas as well as on the recessed areas of the acceptor substrate with an increasing amount of spatter. At even higher fluences (>1 J/cm^2), significant chromium vaporization was observed. On the other hand, experiments using laser fluences lower than ~ 200 mJ/cm^2 (i.e., below the melting threshold of a 30 nm Cr thin film[3]) failed to transfer the Cr nanopatterns. Finally, the transferred Cr nanodots were used as an etch mask to complete 3D structure fabrication. Figure 3 shows the 100 nm high nanopillars on the protruded area of a microwell obtained after etching into SiO_2.

In order to understand the underlying physics in the LA-nTP process, a simple two-dimensional numerical model was developed to solve the heat conduction equation using COMSOL MULTIPHYSICS© and evaluate the spatial and temporal temperature profiles at the donor support/Cr/acceptor substrate interfaces. The temperature dependences of all the thermal properties of the materials involved in this process were taken into account in the model whenever available. The heat conduction of the surrounding air was also considered. The laser intensity was assumed to have a constant radial profile. Figure 4 shows the simulated transient temperature distributions of the interfaces of interest. As expected from the experimental observations, at the end of the laser pulse (full duration $\tau_p = 15$ ns), a maximum temperature of about 3000 K, i.e., the boiling point of Cr, is reached at the irradiated Cr nanodots/quartz interface (solid line) (note that due to the very large latent heat of vaporization of Cr, its vaporization should be negligible). Since the optical absorption depth of Cr ($\alpha^{-1} = 12$ nm) (Ref. 2) is approximately half of the nanodots thickness and its thermal conductivity is high, the temperature within each Cr dot is uniform ($\sim 99\%$). For the metal sandwiched between both surfaces, heat dissipation occurs also via conduction through the acceptor substrate, leading to lower maximum temperatures (~ 2180 K) at both interfaces (dashed line) at the end of the

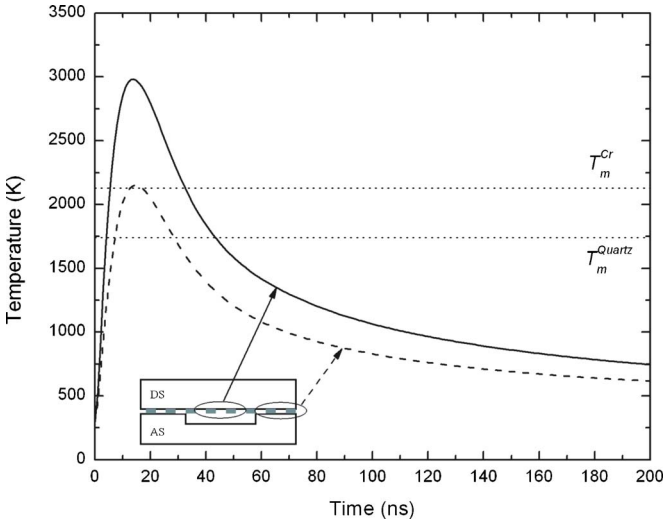

FIG. 4. (Color online) Simulation results of the transient temperature distributions at the DS/Cr interfaces, when the Cr nanodots are (i) not in contact with the AS but surrounded by air (solid line) and (ii) sandwiched between the DS and the AS (dashed line) (DS: donor support, AS: acceptor substrate, T_m^{Cr}: melting point of chromium, and T_m^{quartz}: melting point of SiO_2). The laser pulse is characterized by a duration of 15 ns and a fluence of 350 mJ/cm^2.

laser pulse. It can be noted that the direct contact with the very hot molten Cr nanodots causes the silica surfaces to be heated above the SiO_2 melting temperature (T_m^{quartz}), up to a thickness of $\sim$20 nm below the surface (not shown here). After the laser pulse is switched off, the temperature at both interfaces drops rapidly below T_m^{quartz} within a few tens of nanoseconds. This is in excellent agreement with the experimental observations made above.

Based on the experimental results and the simulated temperature profiles, we believe that two complementary physical mechanisms are responsible for the transfer of the Cr nanodots using LA-nTP. First, the adhesion strength between the Cr nanodots and the quartz support can be weakened by the formation of the silica liquid where many silicon-oxygen bonds might be broken. The detachment of the Cr nanodots could also be favored by the large difference between the thermal expansion of Cr and quartz, which can result in mechanical stress at the donor support/Cr interface. Secondly, chromium thin films are known to adhere well to SiO_2 substrate and probably react with it to form chemical bonds. Cros *et al.*[4] have established that Cr atoms in contact with a strained SiO_2 surface (such as annealed at 800 °C) induce Si–O bond breakage with release of silicon atoms which tend to segregate towards the free surface forming a Cr-rich intermixed layer. Good adhesion of the Cr nanodots via chemical bonding to the less strained acceptor substrate surface might further favor the detachment, while on the noncontact area Cr remains on the donor support.

In conclusion, we have developed a laser-based process for fast printing of nanofeatures, named laser-assisted nanotransfer printing (LA-nTP). Using this technique, we have transferred chromium nanodot array onto a prepatterned thermal SiO_2 surface and used it as an etch mask to complete the fabrication of 3D nanostructures. The transfer mechanism, which occurs over only a few tens of nanoseconds (essentially the melting duration), is believed to be the result of two complementary mechanisms: weakening of the adhesion strength to the quartz donor support via melting and chemical bonding to the acceptor substrate. Undergoing work aimed to investigate the use of different metals films and substrates in LA-nTP will provide additional information allowing to identify the underlying mechanisms for the physical transfer.

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