Nanotechnology **21** (2010) 045303 (5pp) doi:10.1088/0957-4484/21/4/045303

Ultrafast direct imprinting of nanostructures in metals by pulsed laser melting

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Received 18 September 2009, in final form 23 November 2009
Published 16 December 2009
Online at stacks.iop.org/Nano/21/045303

Abstract

We report a method of one-step direct patterning of metallic nanostructures. In the method, termed laser assisted direct imprinting (LADI), the surface of a metal film on a substrate is melted by a single excimer laser pulse and subsequently imprinted within ∼100 ns using a transparent quartz mold, while the substrate is kept at a low temperature and in a solid phase. Using LADI, we imprinted gratings with ∼100 nm linewidth, 100 nm depth, and 200 nm pitch, as well as isolated mesas of ∼20 μm size, in Al, Au, Cu and Ni thin films. We found that the quartz mold was able to imprint metals even at temperatures higher than its melting point. The technique could be extended to other metals regardless of their ductility and hardness, and would find applications in photonic and plasmonic device production.

Metallic nanostructures are a key component in many nanoscale devices such as electrodes for molecular electronic devices [1], magnetic devices [2], photonic devices [3], as well as bio-sensors [4–6]. A low cost high throughput patterning of such nanostructure, particularly a direct patterning without etching, is of great importance. Although conventional nanoimprint lithography (NIL) has demonstrated low cost and high throughput patterning [7, 8] with a high resolution of sub-5 nm [9, 10], they cannot directly pattern nanostructures on a metal surface.

Direct patterning of metal structures by transfer-printing or imprinting without melting the metals have been reported previously. Kim *et al* used a hard silicon mold to press into a metal film on a substrate with a high pressure of 290 MPa that fractured the metal film at the mold pattern edge; and they then peeled off the metal and transfer-printed it to another substrate, achieving sub-micrometer resolution [11]. Yu *et al* fabricated Ag metal electrodes for organic light emitting devices by a transfer-printing with a polydimethylsiloxane (PDMS) stamp, which peels off the portion of the metal film that is in contact with the protruded PDMS patterns [12]. However, it has a low resolution of 13 μm and a low yield that depends on the peel direction. Buzzi *et al*, Pang *et al* and Hirai *et al* applied ultra-high pressures of several hundred MPa to directly imprint a solid metal at room temperature [13–15]. Chen *et al* and Chuang *et al* used a mold having a sharp geometry to deform or imprint (penetrate) metal thin films (<50 nm) deposited on a soft polymer bottom layer at pressure of 10–20 MPa and temperature slightly lower than the glass transition temperature of the bottom polymer [16, 17]. The above methods suffer from poor patterning resolution and are limited to ductile metals because, during the patterning, the metals are in the hard solid phase.

Recently, Ko *et al* has presented the imprint of Au nanoparticle solutions using a special solvent [18, 19]. After nanoimprint, conducting Au structures were resulted by melting the 1–3 nm Au nanoparticles at a moderate temperature. However, the resolution of this process is shown to be only ∼250 nm; and the Au structure after annealing, though conductive, would not be pure with residual solvent and the protecting self-assembled monolayer (SAM) incorporated.

Here we present a novel method of direct imprinting of metal nanostructures using a pulsed laser that can melt the thin metal film. The most prominent feature of this technique is that it is a one-step patterning process—it replaces the steps of

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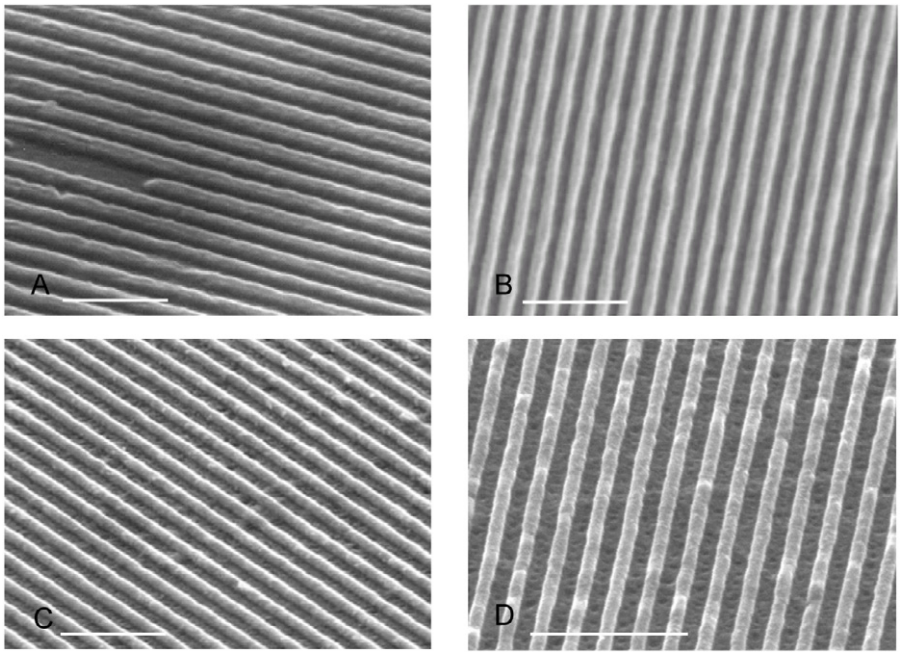

Figure 1. SEM images of 200 nm period metal gratings patterned by LADI. (A) Al, laser fluence 0.22 J cm^{-2}; (B) Au, 0.53 J cm^{-2}; (C) Cu, 0.24 J cm^{-2}; (D) Ni, 0.41 J cm^{-2}. Scale bar is 1 μm.

resist patterning in lithography, subsequent pattern transfer by etching, and resist removal all by one single simple step. In addition, as molten metal has very low viscosity (same order as that of water), this technique can pattern metal within some 100 ns. It can also anneal the patterned metallic nanostructures.

This method is similar to our previous work in laser assisted direct imprinting (LADI) of Si nanostructures with sub-10 nm resolution [20]. Briefly, a thin metal film of 200 nm thick was deposited on a quartz substrate by e-beam evaporation. A mold made in quartz that contained a uniform 200 nm period grating was placed on top of the metal film. The pressure between the mold and the substrate was applied by sandwiching them between two large press plates held by springs. Next, a single laser pulse passed through the quartz mold which is transparent to the laser, and melted the metal film; and the quartz mold imprinted nanostructures into the molten metal. Once the molten metal re-solidified, the mold was separated from the substrate.

We used XeCl excimer laser from Lambda Physik (Model number COMPex 102) with 308 nm wavelength and 20 ns FWHM pulse duration. Excimer laser was chosen because it has high photon energy with strong optical absorption (absorption length ∼10 nm) in most metals. As a result, the laser energy is deposited only onto the metal film with little heating to the substrate when the laser pulse is short. An excimer laser also has relatively poor coherence (duo to a larger number of lasing modes—as many as 10^5 transverse modes [21]) that diminishes interference effects.

A 200 nm period quartz grating mold was duplicated by nanoimprint lithography, liftoff and reactive ion etching from a master mold, which was fabricated by interference lithography with uniform grating pattern over an entire 4″ wafer. The high purity quartz mold absorbs negligible laser energy at 308 nm wavelength. The substrate to be patterned was prepared by e-beam evaporation of 200 nm thick of the desired metal (Al, Ni, Au or Cu) with 5 nm thick Cr adhesion layer (the melting point of Cr is higher than the four metals studied here). The quartz mold was cut into a number of 1 mm^2 quartz pieces, which is smaller than the 2.5 × 2.5 mm^2 excimer laser spot size in order to ensure that the entire substrate area below the mold gets melted during the LADI process.

The imprints were conducted under a vacuum of better than 200 mTorr to remove the air trapped between the mold and the substrate. After imprint, the mold stuck slightly to Al and Ni films, but it could still be separated from the substrate without breaking the mold or peeling off the metal films. The mold did not stick to Cu and Au films. Furthermore, the grating pattern on the mold was not damaged because SiO_2 is mechanically harder with higher melting point than the metals being patterned, hence the mold can be used repeatedly.

Figure 1 shows SEM images of 200 nm period Al, Au, Cu and Ni gratings with ∼100 nm linewidth imprinted by LADI. Only one pulse was used to melt and imprint those metals at a fluence of 0.22, 0.53, 0.24 and 0.41 mJ cm^{-2} for Al, Au, Cu and Ni, respectively. We found that multiple pulses up to 50 pulses had insignificant effects to the imprint results. As shown in the figure, although 100 nm features in metal were imprinted, the resolution was not near the sub-10 nm level as had been achieved in LADI of crystalline silicon [20]. This is partially due to two factors: (1) silicon expands 8.6% when re-solidified, which might help to press the un-solidified silicon to fill the void near the sharp corners; whereas Al, Au, Cu and Ni shrink 11–12% during re-solidification, which draws the un-solidified metals back from the sharp corners and thus results in an unfilled corner and rounded profile; and (2) the surface tension of molten silicon (0.78 N m^{-1} at its melting

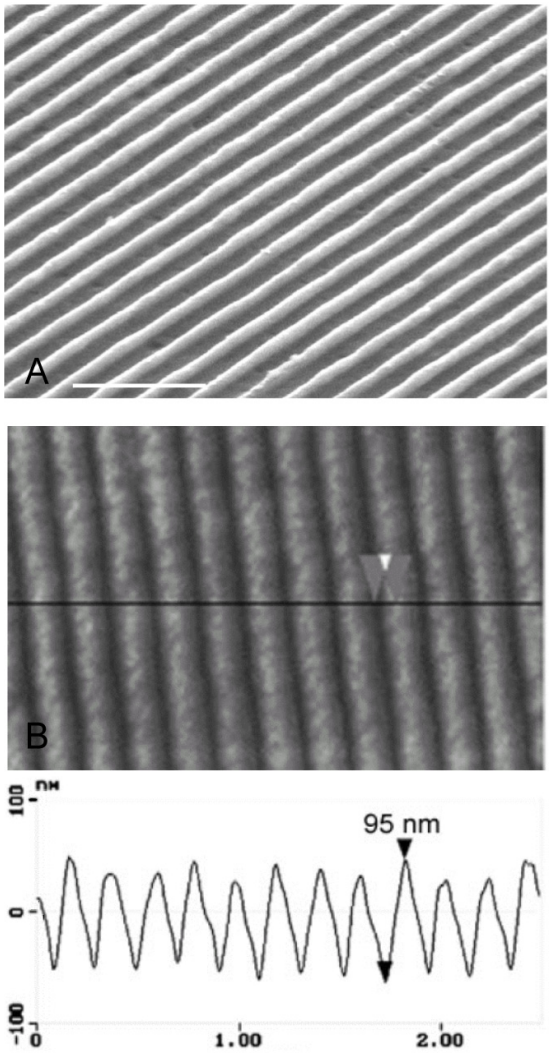

Figure 2. A 200 nm period Ni grating patterned by LADI with laser irradiation from the substrate at laser fluence of 0.60 J cm^{-2}. (A) SEM image; (B) AFM (atomic force microscope) image showing an average trench depth of 90 nm with about 10 nm fluctuation, close to the trench depth on the mold (100 nm). Scale bar is 1 μm.

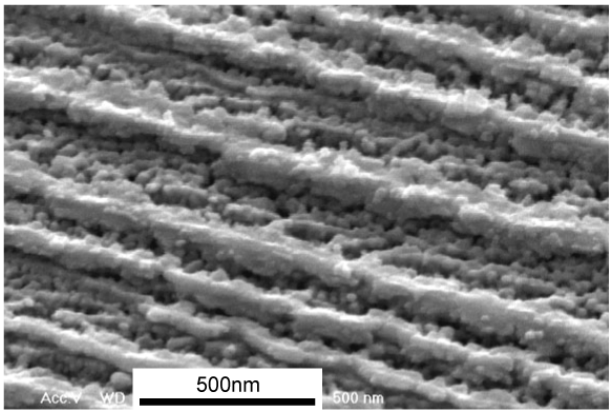

Figure 3. LADI of W using a 200 nm period quartz grating mold at laser fluence of 0.41 J cm^{-2}.

Table 1. Thermal and fluidic properties for the metals studied, together with the properties for SiO_2 and H_2O for comparison. Surface tension and viscosity are calculated from [22].

	Al	Au	Cu	Ni	SiO_2/H_2O
Melting point (K)	933	1338	1358	1726	1883 (SiO_2)
Surface tension at T_{melt} (N m^{-1})	0.87	1.15	1.33	1.80	0.074 (H_2O)
Viscosity (cp) (temperature)	1.38 (933)	5.16 (1373)	3.62 (1438)	4.63 (1727)	0.911 (H_2O)

point) is lower than molten metals (see table 1), so it is easier to imprint. We believe that here the volume shrinkage plays a major role, due to which the trench cannot be fully filled no matter how high a pressure is applied to overcome the surface tension. Besides front-side irradiation (laser beam passes from the mold to the substrate), metal can also be patterned by laser irradiation from the substrate side if the metal is deposited on a transparent substrate with a film thickness low enough (e.g. $<$300 nm) to be melted entirely, as seen in figure 2 that shows an average trench depth of 90 nm with about 10 nm fluctuation, close to the trench depth on the mold (100 nm).

We have also attempted to imprint tungsten. We found that it could be melted readily by a single laser pulse, but it could not be patterned with well defined gratings using a quartz mold, as shown in figure 3. This is likely because: (1) tungsten's melting point is 1800 K higher than that of quartz, hence quartz will be melted (softened) during LADI of W; (2) molten tungsten's surface tension is relatively high, nearly twice that of Cu, thus more difficult to imprint; (3) solid tungsten has a high Young's modulus E, three times that of Cu, leading to $>3\times$ higher thermal stress (equal to $E(\Delta L/L)$, with $\Delta L/L$ being thermal expansion between room temperature and melting point). Because of the high thermal stress, W film was found to crack after the LADI process.

Besides nanoscale features, LADI is also capable of patterning isolated metal mesas and trenches having size of order 10 μm. Figure 4 shows mesas of Au and Cu with 17 μm side length and 100 nm height patterned by LADI. It was found that features of several tens of micrometer size could not be patterned using a single laser pulse. However, theoretically a large pattern can always be achieved by using multiple pulses.

The minimum applied pressure necessary for squeezing the molten metal into the trenches is determined by the surface tension σ and has order of σ/W with W as trench width. As seen in table 1, liquid metals have surface tension much higher than that of water, necessitating a high pressure for filling narrow trenches. However, considerably lower applied pressure would be sufficient for patterning metals by LADI if: (1) the molten metal partly wets the SiO_2 substrate; and/or (2) the mold consists of sparse protruded patterns to create sparse recessed metal features (such as a periodic hole array having diameter $\sim$100 nm and pitch 500–600 nm in Au for extraordinary optical transmission devices [6]), because the effective local pressure at the protruded mold features is significantly higher than the applied pressure (applied force divided by wafer surface area).

For LADI at $\lambda = 308$ nm the characteristic optical penetration depth (equal to $\lambda/4\pi k$, where k is the imaginary

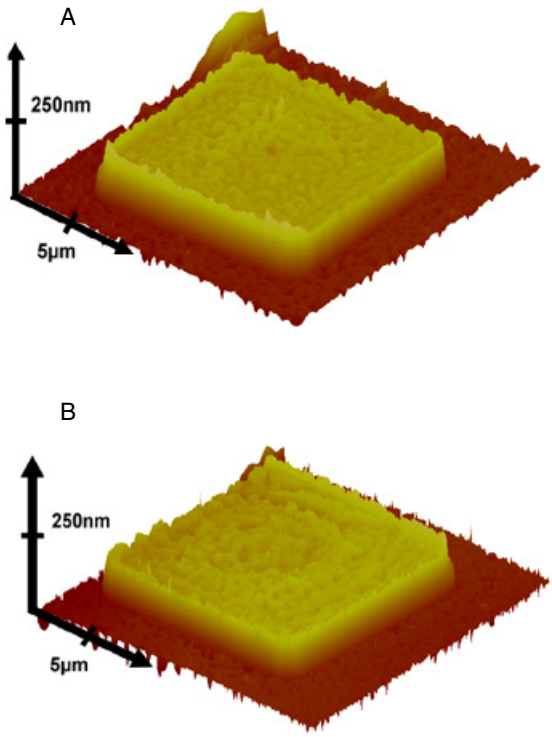

Figure 4. AFM image of isolated mesas patterned by LADI. The mesas have a length on each side of 17 μm, and a height of 100 nm. (A) Au, laser fluence 0.45 J cm^{-2}; (B) Cu, 0.45 J cm^{-2}.
(This figure is in colour only in the electronic version)

part of the refractive index) is 7–14 nm for the metals, therefore almost all the laser energy was absorbed by the top thin layer of the 200 nm thick metal film. As the quartz wafer is transparent, the laser energy is first absorbed by the metal film and then transferred to the SiO_2 substrate and mold by thermal conduction to a characteristic depth of ∼150 nm (equal to $\sqrt{D\tau}$, where D is the thermal diffusivity equal to ∼1.1 × 10^{-6} m^2 s^{-1} for SiO_2, and τ is pulse duration equal to 20 ns) at the end of the pulse. The reflectivity at the quartz surface is about 0.04, and that at the quartz/metal interface is calculated and listed in table 2. Also listed in table 2 is the calculated energy absorbed by the metal film taking into consideration of light reflection at the quartz surface and the quartz/metal interface and heat loss to the substrate and mold (estimated to be ∼0.06 J cm^{-2}, equivalent to the energy needed to heat up a 200 nm SiO_2 film to 1500 K), and the calculated energy needed to heat up and melt 200 nm *freestanding* metal film. From table 2 we can see that: (1) or Cu and Ni, the calculated absorbed laser energies by the metal films are very close to the energies needed to melt them; (2) or Al, it is much lower (even become negative) than the needed energy, implying that the actual reflectivity at the SiO_2/Al interface is far below the calculated reflectivity of 0.90. The actual reflectivity should be <0.5, and this low value is probably due to Al oxidization during film deposition and surface roughness; and (3) for Au, the absorbed energy is high enough to heat up the Au film beyond the melting point of SiO_2, suggesting that the quartz mold, even though molten, can still imprint the Au film (which is due to quartz's extremely high viscosity, see below).

Table 2. Comparison of absorbed laser energy and melting energy for a 200 nm thick metal film. The absorbed energy is derived from the experimental laser energy taking into consideration of optical reflection and heat loss to the substrate and mold. The melting energy is defined here as the energy needed to heat up and melt a freestanding film. Calculations are based on the data from [22–24].

	Al	Au	Cu	Ni
Laser fluence used (J cm^{-2})	0.22	0.53	0.24	0.41
Reflectivity at SiO_2/metal	0.90	0.26	0.27	0.28
Absorbed energy (J cm^{-2})	−0.04	0.32	0.11	0.22
Melting energy (J cm^{-2})	0.06	0.08	0.12	0.20

The maximum feature size that can be patterned by LADI depends on how far the molten metal can flow before re-solidification. For a rough estimation, we first consider only the effect of viscous force by assuming that a steady flow develops momentarily at $t = 0$ (i.e. ignore inertial force). For simplicity, we also assume that the mold has a periodic grating structure. Then the maximum grating half pitch L_1 that can be patterned (trench fully filled) before the liquid metal solidifies is given by [25, 26]:

$$L_1 = h\sqrt{\frac{P\tau}{\mu}} \tag{1}$$

where h is the metal film thickness (200 nm), P is the applied pressure (order 10 MPa), μ is the viscosity, and τ is the melting duration (∼200 ns [20]) that depends on laser fluence. The effective pressure is actually lower than the applied pressure by σ/L for the case of total de-wetting between the molten metal and the substrate, which is negligible for $L > 1$ μm. As seen in table 1, the viscosity of molten Au and Cu is around 4 cp (∼5× that of wafer), leading to $L_1 \sim 5\mu$m. To pattern isolated metal mesas, the liquid flows from four sides to fill a square-shaped hole in the mold, so the maximum patternable mesa size should be roughly doubled to ∼10 μm, which qualitatively agrees with the experiment (17 μm). Moreover, it is interesting to see how far molten SiO_2 can flow under similar conditions. For example, its viscosity at 2200 K is 8×10^7 cp (a very tacky 'liquid'), 7 orders higher than that of Au and Cu, leading to a calculated L_1 of only ∼1 nm if assuming a top 200 nm SiO_2 layer is molten. This explains why the quartz mold can be used to pattern a metal (here Au) at temperature slightly higher than its melting point, though the mold can no longer be used repeatedly for many times.

Next, to estimate the inertial force which decides how fast the steady flow develops, it is assumed that the liquid metal is inviscid ($\mu = 0$) for simplicity. Then the maximum grating half pitch L_2 that can be patterned before the liquid metal solidifies is given roughly by [27]:

$$L_2 = \sqrt{\frac{P}{\rho}\tau} \tag{2}$$

where ρ is the liquid metal density. The density for liquid Au and Cu is 17.3×10^3 and 8.0×10^3 kg m^{-3}, leading to $L_2 \sim 5$ and 7 μm, respectively, which is of the same order as L_1.

Therefore, both viscous force and inertial force are important in determining the overall maximum feature size that can be patterned by LADI.

In conclusion, we demonstrated a simple and ultrafast molding technique for nanostructuring metals using pulse laser melting. Compared to other contact printing or imprinting techniques for pattering metals, LADI gives higher resolution without the need of ultra-high pressure of several hundred MPa that may lead to mold damage, and the embossing time is only a few hundred nanoseconds. Moreover, the current method doesn't need ultra hard and strong molds, and can pattern most metals regardless of its ductility and hardness. The major challenge for LADI is the scaling up of the process that depends on the availability of high power pulsed lasers having wafer-size power uniformity. The metal structures fabricated by LADI could find applications in photonic and plasmonic devices including bio-sensors.

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