Ultrafast patterning of nanostructures in polymers using laser assisted nanoimprint lithography

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We propose and demonstrate a nanopatterning technique, laser-assisted nanoimprint lithography (LAN), in which the polymer is melted by a single excimer laser pulse and then imprinted by a mold made of fused quartz. LAN has been used to pattern nanostructures in various polymer films on a Si or quartz substrate with high fidelity over the entire mold area. Here we show 200 nm pitch gratings with 100 nm linewidth and 90 nm height. The entire imprint from melting the polymer to completion of the imprint is less than 500 ns. The mold has been used multiple times without cleaning between each imprint. LAN not only greatly shortens the imprint processing time, but also significantly reduces the heating and expansion of the substrate and mold, leading to better overlay alignment between the two. © *2003 American Institute of Physics.*
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Nanoimprint lithography (NIL) has been demonstrated as a low cost, high throughput patterning technique with sub-10 nm resolution.[1,2] It has great potential as a candidate for next generation lithography. In NIL, either thermal-plastic or UV-curable resists can be used.[3] UV–NIL can be used to avoid heating the resist, but it often needs multiple resist layers and multiple etching steps, thus increasing the cost. Traditional thermal-based NIL, on the other hand, is good for patterning both two-dimensional and three-dimensional nanostructures with a single resist layer;[4] however, heating the resist is often slow and creates a thermal expansion difference between the mold and substrate that could result in misalignment. Such misalignment has been avoided by employing a mold and substrate made of the same material.[5]

In this letter, we describe a nanopattening technique, laser-assisted nanoimprint lithography (LAN), which combines the advantages of traditional thermal-based NIL and laser-assisted direct imprint.[6] We demonstrate that LAN is capable of producing nanostructures in various polymers on different substrates by using only one excimer laser pulse and that the entire process from melting the polymer to completion of imprint is less than 500 ns. Furthermore, the laser melting of polymer reduces the polymer viscosity and, hence, reduces imprint pressures. Finally, numerical simulation shows that there is negligible heating of the substrate and mold.

In our LAN experiments, a single XeCl excimer laser pulse (308 nm wavelength and 20 ns pulse duration) passes through a quartz mold (which does not absorb the laser energy because it has a band gap larger than the photon energy) and melts a 200 nm polymer film on a substrate, during which time the mold is immediately imprinted into the polymer.

In making quartz molds, 200 nm pitch gratings on a Si master mold were transferred to a 2 in. fused quartz wafer using traditional thermal-based NIL and reactive ion etching. The quartz wafer was then diced into 1 mm×1 mm pieces with 200 nm period gratings (100 nm line/spacing, 90 nm trench depth) over the entire mold. The molds were treated with an antiadhesion coating for better mold release after the imprint.

We have tested LAN on various polymers, for example, polystyrene, poly(methylmethacrylate), and nanoimprint resists (NPR series made in house) on different substrates. All resist films were baked at 60–70 °C for 30 min to drive out residual solvent.

In LAN we have observed that a single laser pulse was sufficient to imprint the nanopatterns on the mold into the polymer with high fidelity. For example, with a laser fluence of at least 0.35 J/cm^2, uniform gratings of 200 nm period in the mold [Fig. 1(a)] were transferred completely to a thermal-plastic resist, NPR-69, which has a glass transition temperature of about 100 °C. The replicated gratings had vertical sidewalls and flat surfaces and bottoms [Fig. 1(b)], identical to those in the mold. Besides NPR-69, excellent pattern transfer by LAN was also observed in other polymers, but at different laser fluences depending on the glass transition temperature and laser absorbance of the polymer. In testing LAN with another NIL polymer, NPR-46 for instance, a single laser pulse with a fluence of 0.56 J/cm^2 was used. Examination using an atomic force microscope (AFM) revealed that the polymer grating height is the same as the mold trench depth (90 nm), indicating complete pattern transfer from the mold to the polymer (Fig. 2). Based on the earlier results, it can be concluded that even with such a short heating and imprinting time, LAN has produced high-fidelity transfer of nanostructures as good as that in traditional thermal-based NIL.

We also tested LAN using different substrates. For NPR-69 on a quartz substrate, we found that at least 0.5 J/cm^2 laser fluence was needed for a good imprint, higher than that on a Si substrate (Fig. 3). The difference in required fluence is attributed to the difference in the laser absorbance

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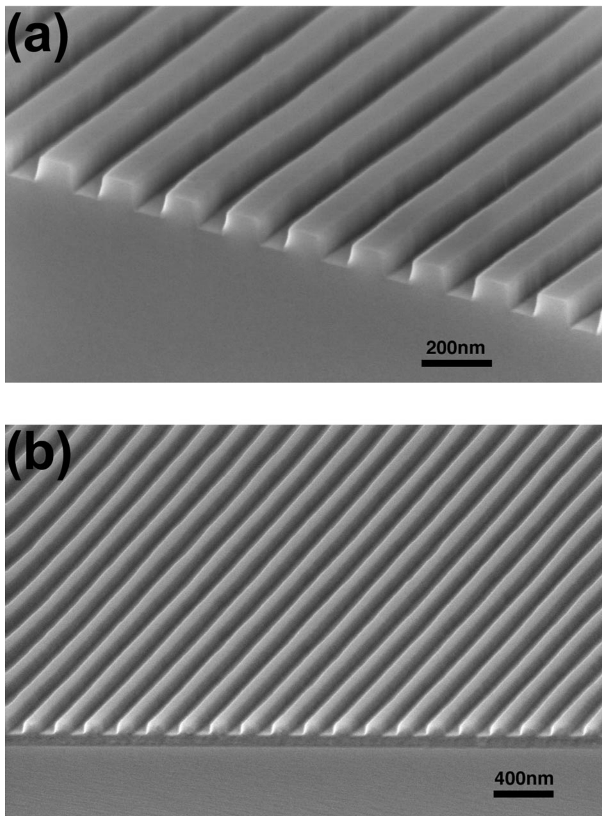

FIG. 1. (a) Scanning electron microscope (SEM) image of the 200 nm period grating mold made from quartz. (b) NPR-69 gratings on a Si substrate produced by LAN with a single laser pulse of 0.4 J/cm^2. The gratings have a linewidth of 100 nm and height of 90 nm.

of polymer on different substrates. Using a simple multi-interface reflection model,[7] we found that for a 200-nm-thick polymer (NPR-69) with an absorption coefficient of about 8×10^{-4} nm^{-1}, the fractional absorption is about 21.4% on a Si substrate, and 14.3% on a quartz substrate. In these calculations, the refractive indices for Si and quartz at 308 nm wavelength were taken from a handbook,[8] and the refractive index of the polymer was measured using an ellipsometer. The difference in polymer absorption is due to larger reflectivity at the Si-polymer interface than at the quartz-polymer interface. The other possible reason for the different fluences is that the quartz substrate does not absorb the 308 nm laser pulse, but a Si substrate does and transfers the heat to the polymer on it. Hence, incident energy was used more efficiently for polymer on a Si substrate.

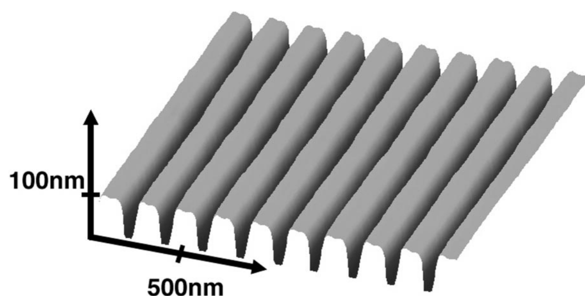

FIG. 2. AFM image of NPR-46 gratings produced on a Si substrate. The height of the gratings is 90 nm, which corresponds exactly to the depth of the trench in the mold. A single laser pulse with a fluence of 0.56 J/cm^2 was used.

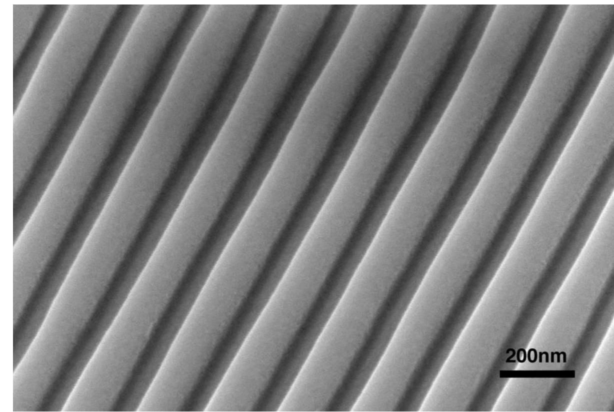

FIG. 3. SEM image of NPR-69 gratings made on a quartz substrate by a single laser pulse of 0.5 J/cm^2.

We also found that in LAN the molds with antistick coating could be used repeatedly without loss in the grating quality [Figs. 4(a) and 4(b)]. The imprinted area could be as large as that of the mold and was quite uniform.

The LAN process has several advantages over conventional thermal imprint. One is a much shorter processing time (hundreds of nanoseconds). The other is that the heating of the substrate is greatly reduced, hence, avoiding misalignments due to the thermal expansion mismatch of the mold and the substrate, which is a problem for multilevel electronic device fabrication.[9] For quartz substrates, the substrate temperature remains nearly unchanged during LAN, because there is no direct absorption of the laser energy and poor heat

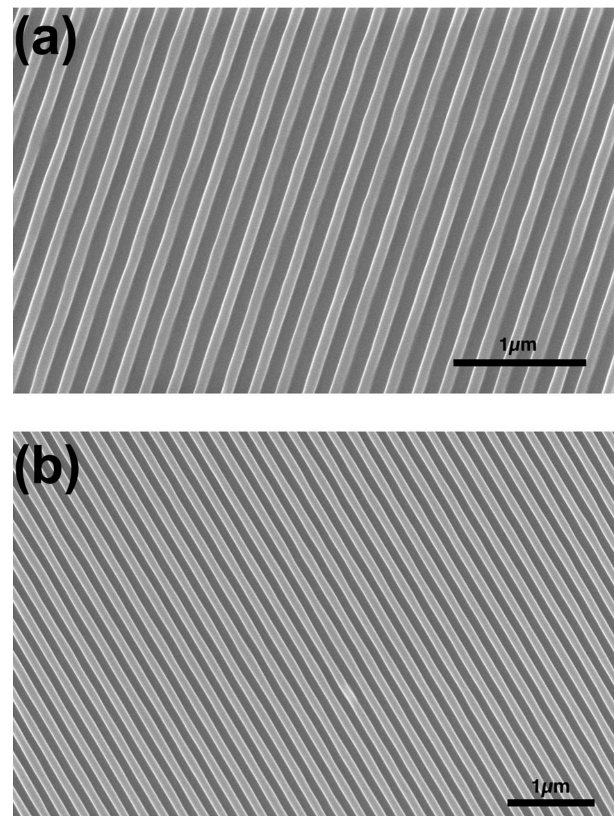

FIG. 4. SEM images of 200 nm NPR-46 period gratings produced on a Si substrate by a single laser pulse (0.56 J/cm^2) using the same mold. (a) Imprint result after mold is used for the first time and (b) after the third time. There is no obvious difference in grating quality in the two pictures.

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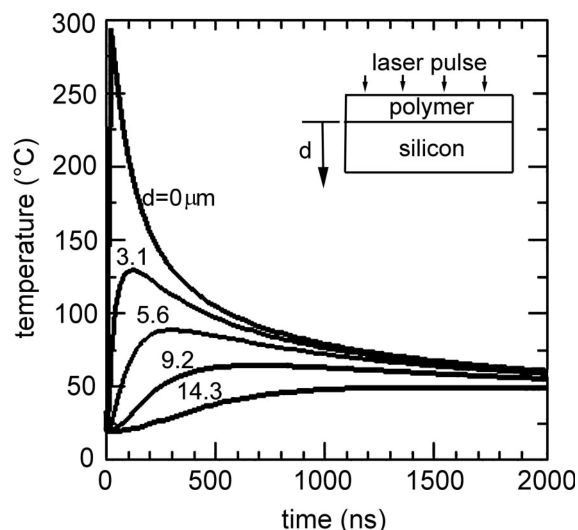

FIG. 5. Simulation results of temperature evolution in the surface layer of a Si substrate after the incidence of a single laser pulse ($0.4\ \mathrm{J/cm^2}$). Each curve represents the temperature as a function of time at different distances from the Si surface. The inset shows the model geometry in which we assume a 200 nm polymer film on a 500 μm Si substrate.

conduction (two orders of magnitude less than Si).[10] For Si substrates, numerical simulation was performed to get a better understanding of the substrate heating. In our simulation, the laser fluence was $0.4\ \mathrm{J/cm^2}$ and the thermal diffusion length for Si was calculated using tabulated physical properties[10] to be 1.3 μm for a 20 ns laser pulse. Figure 5 shows the temperature evolution with time at different distances from the Si surface assuming a 200 nm NPR-69 film on top. From the simulation, the following conclusions can be drawn. First, only a 14.3 μm thin layer near the surface (a thickness about 3% that of the Si wafer) was thermally affected during the process while the bulk of the Si wafer remains nearly at room temperature. Second, the Si surface temperature drops below the polymer glass transition temperature (about $100\,^\circ$C) within 500 ns, which means the whole imprint process time was shorter than that. Third, during the imprint process, with a room temperature substrate beneath the surface layer, the lateral thermal expansion in that layer can be efficiently constrained, which is promising for good overlay alignment.

It should be pointed out here that the heating of the Si substrate could be further reduced by simply tailoring the polymer chemical composition to increase laser absorbance of the polymer. For example, according to our model,[7] for a 200 nm polymer film on quartz, an increase of polymer absorption coefficient from $2\times10^{-4}\ \mathrm{nm^{-1}}$ to $1\times10^{-3}\ \mathrm{nm^{-1}}$ would result in an increase of fractional absorption from 7.5% to 18.3%.

Finally, light sources other than an excimer laser can be used in LAN, which may open up opportunities for large area ultrafast thermal-based NIL.

In summary, LAN is an ultrafast nanopatterning technology which will significantly reduce misalignment between the mold and substrate during NIL. In LAN, the imprint time can be as short as 500 ns and the mold can be used multiple times without cleaning between each imprint. This method could be scaled to full wafers provided that large area light sources are available. LAN can also be used in fabricating some organic electronic and optical devices.

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