Near-field scanning optical microscopy based nanostructuring of glass

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Abstract. Nanofabrication, at lateral resolutions beyond the capability of conventional optical lithography techniques, is demonstrated here. Femtosecond laser was used in conjunction with Near-field Scanning Optical Microscopes (NSOMs) to nanostructure thin metal films. Also, the possibility of using these nanostructured metal films as masks to effectively transfer the pattern to the underlying substrate by wet etching process is shown. Two different optical near-filed processing schemes were studied for near-field nanostructuring. In the first scheme, local field enhancement in the near-field of a scanning probe microscope (SPM) probe tip irradiated with femtosecond laser pulses was utilized (apertureless NSOM mode) and as a second approach, femtosecond laser beam was spatially confined by cantilevered NSOM fiber tip (apertured NOSM mode). The minimized heat- and shock-affected areas introduced during ultrafast laser based machining process, allows processing of even high conductivity thin metal films with minimized formation of any interfacial compounds between the metal films and the underlying substrate. Potential applications of this method may be in the fields of nanolithography, nanofluidics, nanoscale chemical and gas sensors, high-density data storage, nano-opto-electronics, as well as biotechnology related applications.

1. Introduction
Nanostructuring of thin films is gaining widespread importance owing to ever-increasing applications in a variety of fields. Recently, scanning probe lithography (SPL) has emerged as an inexpensive and compact tool for nanopatterning of a variety of sample surfaces. Scanning microscopy techniques such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), near-field scanning optical microscopy (NSOM), and further variants thereof, have been extensively used in numerous high-resolution nanostructuring studies, to manipulate single atoms, and also as effective all-inclusive nanofabrication tools. Various non-optical phenomena based on SPL have been explored in the past that include mechanical indentation, localized oxidation and current injection, pulsed or continuous voltage techniques and conducting probe methods [1]. Lithographic techniques based on NSOM, used in both apertureless [2-4] and apertured modes [5-7] have been investigated. NSOM lithography schemes have involved processes either based on photochemistry (using thin organic resist layers) or on local material ablation (direct writing process) [5-7]. However, most of the studies have focused on surface structuring of films without attempting lithographic feature pattern transfer, possibly due to the shallow depth of the written features.

For the current study, two different near-field schemes were employed to nanostructure the thin metal films and as a subsequent step perform nanolithography. In the first scheme (hereafter referred
to as Scheme A), local field enhancement in the near-field of a SPM probe tip irradiated with femtosecond laser pulses was utilized and as a second approach (hereafter referred to as Scheme B), the femtosecond laser beam was spatially confined by cantilevered near field scanning optical microscope (NSOM) fiber tip. These confined laser beams were used to perform ablation lithography on thin metal layers and by subsequent etching steps, the patterns generated on the top metal masking layers were transferred onto the underlying substrate. The samples used in the experiment were ~8-nm-thick In film deposited on Si substrate and dual-metal layer films consisting of a 13-nm-thick top layer of Au and a 6-nm-thick intermediate layer of Cr (to enhance the adhesion) deposited onto fused quartz substrates.

2. Experimental details

Experimental schematics for the two schemes described earlier are shown in figures 1(a) and 1(b). Using the chirped pulse amplification technique, ultra-short pulses were generated, with ~100 fs full-width half-maximum (FWHM), 800 nm wavelength, and 1 mJ maximum pulse energy. Further, a second harmonic generation crystal was used to generate frequency doubled ($\lambda = 400$ nm) femtosecond laser pulses for use in scheme B.

![Figure 1](image)

**Figure 1:** Schematic diagram for the experimental setup based on (a) local field enhancement underneath a SPM probe tip (Scheme A) and (b) cantilevered NSOM fiber probes (Scheme B).

For the scheme A, the femtosecond laser beam, after necessary attenuation, was focused onto the AFM probe tip using a 175 mm focal length positive lens, producing a 1/e² beam spot diameter of ~74 μm as measured with the knife-edge technique. Details of the experimental procedure for field-enhancement based scheme A have been provided elsewhere [2].

For scheme B, frequency doubled ($\lambda = 400$nm) femtosecond laser beam was coupled to the NSOM fiber probes after pulse energy attenuation and measurement using a 5X objective (NA = 0.1) mounted within a standard fiber coupler. Bent cantilevered multimode NSOM fibers, of 500nm aperture sizes, fitted onto a commercial NSOM system (by Nanonics Imaging Ltd) were used in the current experiment. To maximize the light transmission through an optical fiber, it was critical to collinearly align the laser spot to the core of the fiber in the coupler. To aid the alignment process and measure the energy output from these fibers a pico-joulemeter was used. The transmission efficiency curves for the various fibers were obtained by placing a high-gain amplified detector just before the fiber coupler to collect the input energy and a pico-Joule meter at the exit of the fiber tip.

3. Experimental nanolithography results

Experimental results for the nanomachining of the metal thin films and their subsequent use as effective masks for feature transfer are discussed here. Figure 2 (a) shows nanocrater formation on 8-nm-thick In film, using scheme A, with input laser fluence equal to 0.035 J/cm². The corresponding cross-section profile, shown in figure 2(b), reveals crater depth greater than the thickness of the In layer, exposing nanometer-sized spots on Si. Figure 2(c) shows the cross section profile of nanochannels formed on 13-nm-thick Au/6-nm-thick Cr dual-layer film deposited on quartz, using scheme A, with input laser fluence equal to 0.043 J/cm². Here again the exposure of the underlying
quartz substrate is clearly seen. Although the width of the nanocrater (in figure 2 (b)) and the nanochannels at the top surface are ~ 60 nm and ~75 nm respectively, the widths of the exposed substrates underneath appear to be less than 10 nm. This suggests that by manipulating the surface chemistry, metal thin films can be used as masks for subsequent processing.

Figure 2: Nanomachining results based on scheme A for the formation of (a), (b) nanocrater on In film deposited on Si, (c) nanochannels on Au/Cr dual-layer deposited on quartz for laser fluence equal to 0.035 and 0.043 J/cm², respectively. The cross-section profiles shown in (b) and (c) indicate that the features are deeper than the thickness of the masking metal films thus effectively exposing the underlying Si and quartz substrates, respectively.

Figure 3 shows the representative schematic for the process sequence involved in the nanomachining of the metal thin films, using scheme B. An input laser fluence of 3.2 J/cm² was used for defining the ablation crater and subsequently wet etching was employed for transferring the features formed on the metal films to the underlying transparent quartz substrate. To briefly summarize, the process involved the following steps: (a) using single laser pulses, patterns were made on pre-marked masking metal layers (as shown in figure 3(a)), (b) after cleaning and characterization with an AFM, wet-etching was performed on the sample by immersing it in 10% HF solution (diluted in DI water) for a duration of 2 minutes to transfer the feature into the underlying quartz substrate. The sample was then thoroughly rinsed in DI water to remove any left-over etchant and was moved to an AFM for scanning the etched regions to note the increase in the depth of the craters (this step is depicted in figure 3(b)), (c) now the masking layers were stripped off by immersing the sample in standard Au and Cr etchants sequentially for time durations of 5 minutes each. These were long enough to completely etch away the entire thickness of the metal layers to obtain the final transferred feature on quartz (refer to figure 3(c)).

Figure 3: AFM scans showing the process sequence for the ablation nanolithography of Au+Cr dual-metal layers on quartz substrate, using scheme B, for the case of input laser fluence of 3.2 J/cm². The AFM scans show, (a) crater profile after laser ablation, (b) crater profile after wet etching of the quartz substrate (using HF) and (c) final transferred crater profile on quartz after stripping off the top two masking metal layers (using Au and Cr etchants).

Selected results from the parametric study using Scheme B are shown in fig. 4 wherein the laser fluence applied on the sample surface was varied as a parameter. AFM crater profiles for the cases of input laser fluence of 2.8 J/cm², 2.9 J/cm², and 3.2 J/cm² are shown in fig. 4 (a), (b) and (c) respectively. For the current study the smallest crater profile obtained had a Full Width Half Maximum (FWHM) lateral dimension of ~90 nm.
Figure 4: Transferred features on the quartz substrate after wet etching through the metal masking layers and subsequent strip-off of the metal films for the cases of laser fluence equal to (a) 2.8 J/cm², (b) 2.9 J/cm², and (c) 3.2 J/cm². The cross-section profiles reveal the dimensions of the produced nanofeatures.

It is noted here that though the top lateral dimension of the inner negative region of the ablated crater in fig. 3(a) is ~300nm, the exposed region on Quartz is much smaller due to the Gaussian-like crater profile which replicates the laser beam profile and is characteristic of laser ablation process. Thus it is possible to expose very small region of quartz by closely controlling the input energy fluence. Further, the use of HF based wet-etching technique in this study was done only to demonstrate the feasibility of using these metal thin films as effective masking layers for NSOM ablation lithography. HF based etching that is an isotropic method effectively enlarges the lateral dimensions of the final obtained crater. However, the issue of resolution loss could be remedied by using alternative dry-etching techniques such as Deep Reactive Ion Etching (DRIE), that allow straight transfer of the pattern from the mask onto the underlying substrate. Further, it is also worth noting that as seen from figs. 3 and 4, the elevated rim structures, that are inevitable in laser ablated craters, were restricted only on the top of the metal masking layer. Hence, after strip-off a clean rimless transferred crater profile was obtained. Using NSOM probes of smaller aperture dimensions and thinner metal films could also further reduce the lateral dimensions of the features. The throughput from the current 500nm probes was high enough not only to ablate the entire thickness of the two metal film layers, but also to damage the underlying quartz substrate for the cases of high input laser fluence. Thus, by employing probes of even smaller aperture sizes (which corresponds to lower throughput), it should still be feasible to go through the metal film layer and expose smaller regions on the quartz substrate.

4. Conclusions
Femtosecond laser and NSOM (both apertureless and apertured modes) based ablation lithography was carried out with accuracy and reproducibility. Ablated patterns generated on metal masking layers were effectively transferred on to the underlying transparent quartz substrate. The ability to produce these nanostructures on transparent substrates in a controlled fashion could be beneficial in a number of applications. The possibility of utilizing arrays of probes with necessary switching mechanism could make these schemes attractive as far as the overall throughput is concerned.

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