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Nano slit and dot array pattern of Au on SiO_2 substrates using laser beam lithography

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ABSTRACT

Highly monochromatic coherent light intensity of lasers provides the possibility of fabricating periodic nano-patterns which are needed in many applications. Here, we report 2D grating structure and periodic nano hole and dot arrays fabricated using two laser beam interference lithography. Using this method periodic grating as well as dot patterns have been fabricated with structure size of 50 -100 nm and pitch of 200-300 nm on SiO_2 substrate. The nano-patterns are formed by inverting an array of photoresist posts by a lift-off process and subsequent reactive-ion etching using chromium as an etch mask. The depth of patterns can be tuned simple by laser dose to obtain high aspect ratio gratings. Transmission spectra measured in Au slits shows strong resonance features at 520 and 640 nm. Finite difference time domain simulations are used to estimate the near-field enhancement at the center of the slit pattern. Copyright © 2013 VBRI press.

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Introduction

Creating ordered nanostructures has wide technological demands because they are applicable to photonic crystals [**1**], biology [**2**], magnetic storage [**3**], solar cells [**4**], microelectronics and optoelectronics [**5**] applications. Lithography is a standard technique to fabricate nanostructures referring to a process in which a surface is patterned by first coating it with a material called "resist" then forming a desired stencil pattern in the resist coating, and finally transferring the pattern onto the surface. A variety of energy sources can be used for exposing the resist pattern such as optical photons, x-rays, laser beams or electron beams. Different lithographic techniques include electron beam lithography (EBL) [**5**], focused ion beam lithography (FIB) [**4**], nanoimprint lithography (NIL) [**2**], and laser interference lithography (LIL) [**1**], which are used to generate different nanostructures. Nanosphere lithography (NSP) [**6**], two-photon lithography (2PL) [**7**] and dip pen nanolithography (DPN) [**3**] are also used to fabricate ordered nanostructures. High spatial resolution arbitrary patterns can be achieved using EBL, FIB, 2PL, and DPN, but they do so at high fabrication costs. Two-dimensional large-area structures can be generated using NSP, but only with hexagonal arrays. Surface reliefs with different shaped nanostructures can be achieved using NIL. However, the high cost of a master mask (often made by EBL) needed for NIL stamps and its processing contamination limits the applications to some extent.

Ordered nano patterns of metals such as Au, Ag, Ni, Al have potential applications in spectroscopy and plasmonics. Specifically, effects of near-field coupling on plasmon resonance of metal nanostructures such as binary particles [**8-13**], chains of particles [**14**], and cylindrical wires [**15**] have been subjects of intense research recently. Plasmon resonance in near-field-coupled 2D particle arrays is particularly interesting due to its ability to obtain high field enhancement over large areas [**16-18**]. Such systems are potentially useful in SERS or in exploitation of nonlinear phenomena such as second-order or super-continuum white light generation. Obtaining large enhancement factors over large areas in a uniform and reproducible way is of critical importance for such uses.

Here we report the fabrication of two dimensional structures such as arrays of holes, dots and grids on Si and SiO_2 substrates. A high power laser source was used with suitable beam optics to interfere over a large area from which we chose a uniform area of square centimeter to expose on the photoresist to obtain the grating pattern. For arrays of holes and dots, multiple exposures were done by rotating the same sample. This LIL method is quite impressive for periodic nano-patterning because it offers a relatively simple and low-cost high-efficiency method. This technique has the advantage of providing unlimited depth of focus and large area exposures without requiring complicated and expensive optics. Grating array of 200 nm periodicity was obtained in the initial stage. In this paper I have discussed the potential of LIL along with the large near filed enhancement and transmission of line and dot pattern of Au on SiO_2 substrates.

Experimental

The laser interference technique is based on the production of two coherent beams from a source of a given wavelength. These beams can be produced simply dividing the original beam into two by making the first one pass through a 50/50 beam-splitter (BS). After this BS, mirrors are used in a suitable way in order to produce the interference between them on the target. Before this, each beam passes through a pinhole that forms a spatial filter.

When two mutually-coherent light beams interfere, alternating light and dark fringes with a period determined by the angle between them and the wavelength of the light are produced. This standing waves can be recorded in a photosensitive material, coated on substrate. Calling this half angle θ between two beams, the period (p) of the interference patterns in the x-direction is given by $p = \frac{\lambda}{2 \sin \theta/2}$, where, λ is the wavelength of the laser in the medium that surrounds the substrate (usually air). The depth of focus of this method is dependent on the coherence length of the light and can be of the order of meters or more, compared to micron or sub-micron values for conventional optical lithography systems. Theoretically, the smallest period that can be obtained occurs for θ = 90° and is equal to λ/2. Patterns with periods as small as 165 nm can be obtained with the use of laser light with a wavelength of 325 nm He-Cd laser [**5**]. The patterns are limited by the spatial coherence of the source. In this experiment we config.ured our setup to expose gratings with a period of 200-300 nm using a TEM00 polarized He-Cd laser. The central area about 1cm×1cm was used to print the pattern on the photoresist (PR). The interference pattern can wash out the fringes recorded on PR due to small vibrations during recording. So, the whole setup for interference pattern was on a vibration free table adequately covered from all sides to avoid external disturbances.

Well cleaned n-type silicon and α-quartz of size 10mm x10 mm were deposited with 10-15 nm Chromium layer for an adhesive layer using a thermal evaporation techniques with a vacuum of 10^{-7} mbar. These samples were spin coated with 75 nm of anti-reflecting coating (ARC) layers. This ARC layer provokes the standing waves created by the reflection from the wafer. On the top of it, 80nm of positive photoresist (PR) called Ultra-I 123 I-Line from Rohm and Haas company was spin coated at 4000 rotations per minute. After each spin coating step, the samples were soft baked at 90°C for 90 minutes. Then the samples were ready for exposure at the interference stage. To create line pattern a single exposure was sufficient. The dose of around 70 – 100 mJ/cm^2 was optimized for several experiments. For 2D hole pattern the samples were turned 90° after first exposure. The optimized dose for a hole pattern lies between 70 and 75 mJ/cm^2. If there are higher doses, the structure widths will be reduced. If the exposure is not long enough, it risks the creation of not completely open and irregular structures. After the samples are exposed with interference pattern, it needs to developed using suitable developer. In this case we used Megaposit MF-24 A, for 45 seconds. Then the samples were rinsed with deionized water for a prudent time (about 25-35 seconds) and cleaned with nitrogen immediately. **Fig. 1** shows the cross-sectional SEM image and the corresponding schematic of the samples fabricated using LIL. Always identical samples were made on Si substrates along with SiO_2 substrates to obtain the SEM image easily on Si substrates.

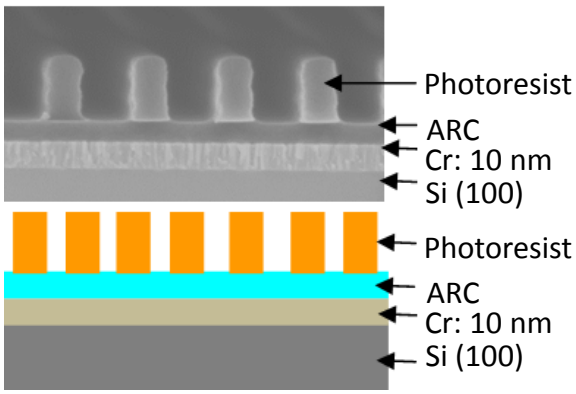

Fig. 1. SEM and corresponding schematic view of the LIL exposed photoresist with 200 nm period after development using Megaposit MF-24 A for 45 seconds.

Once the samples are exposed and the interference pattern has been observed on the PR layer, we need to transfer the pattern to the substrate for the specific application. So it is important to implement the process flow for pattern transfer to a substrate to create nano hole arrays, dot arrays and line arrays. Following are few steps of the process flow we used to create the periodic patterns. The ARC and Cr layer was removed using reactive ion etching (RIE) with suitable plasma. Then 80 - 100 nm of

Au was deposited on the etched samples using thermal evaporation techniques. The optical microscope images were obtained using both transmission and reflection geometry. Transmission spectra were obtained using a conventional UV/VIS/IR spectrometer in the wavelength range of 200-800 nm with unpolarized light and no focusing optics used to the large size of the array.

Results and discussion

The scanning electron microscopy (SEM) images of high resolution grating pattern on PR of 200 nm periodicity, fabricated using LIL technique on Si substrates are shown in **Fig. 2** (a). The SEM images were taken using 2 keV electron energy and a distance of 4 mm working distance to avoid charging effect on PR. The pattern in PR was transferred first into the ARC layer by an O_2 based RIE process. The resulting PR-ARC pattern was then transferred into the 80-100 nm thick Au layer by a Cl_2 based RIE and liftoff. The SEM image of the corresponding grating pattern of Au is shown in **Fig. 2** (b). It has been observed that the lines are not so sharp as compared to PR images because Au film cannot be smooth at the edge by thermal evaporation method.

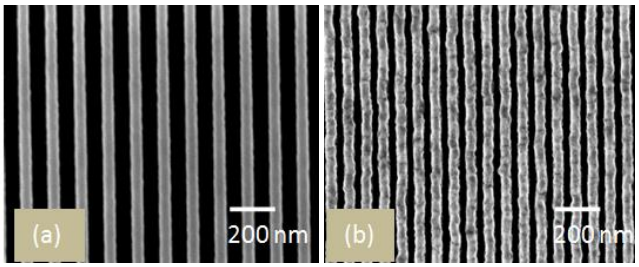

Fig. 2. The 200 nm periodic grating pattern on (a) photoresist patterns, (b) on Au grating patterns after ARC and Cr removal

After the first exposure the sample was rotated by 90 degree and exposed with the same dose to obtain the hole pattern in the PR. **Fig. 3** (a) show the hole pattern for an optimized dose of 70 mJ/cm^2. **Fig. 3** (b) shows the non-uniform hole pattern exposed with lower dose (~ 50 mJ/cm^2).To obtain the dot pattern of Au, 80-100 nm Au was deposited on these hole pattern surface. Then the ARC and Cr layer was removed by liftoff process. The Au dot patterns corresponding to **Fig. 3** (a) and (b) are shown in **Fig. 3** (c) and (d). It has been observed that there is a one-to-one dot pattern observed after liftoff. To know the exact depth of the grating and hole pattern, we have carried out Atomic force microscopy (AFM) shown in **Fig. 4** (a) and (b). The thickness of the deposited Au layer was around 100 nm, determined from AFM micrograph, which matches well with the value measured by thickness monitor of the deposition unit.

The period of the grating pattern can be varied by changing the angle of the two mirrors which changes the angle of the two interfering beams on the PR plane. For spectroscopic application one need high aspect ratio grating. The depth to grating period ratio has to be tuned properly for high aspect ratio grating. The depth of the grating mainly depends on the dose of exposure and also the type of PR used. **Fig. 5** shows the dependence of depth of nano pattern as a function of dose of the laser beam. The depth of the pattern increases linearly along with laser fluences until about 70 mJ/cm^2 for 80 nm Ultra-I 123 I-Line PR. Above this value, the depth on PR remains nearly stable. As we increase the thickness of the PR to 110 nm, the linear part becomes sharper and only after the dose of 90 mJ/cm^2 the complete exposure takes place.

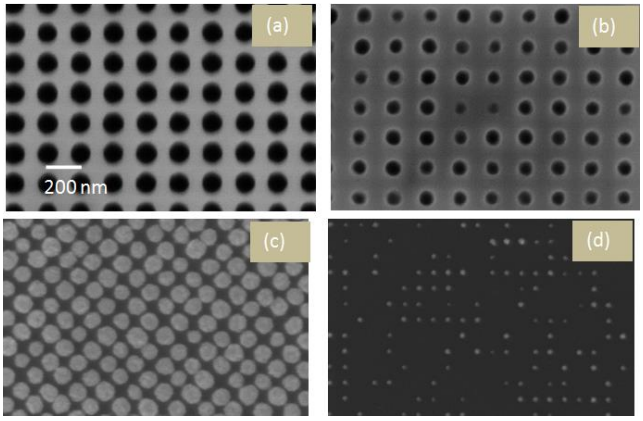

Fig. 3. The hole pattern of 200nm period obtained after LIL double exposure using a laser dose of (a) 70 mJ/cm^2 and (b) 50 mJ/cm^2, (c) and (d) are the corresponding dot pattern after liftoff of Cr and Au deposition.

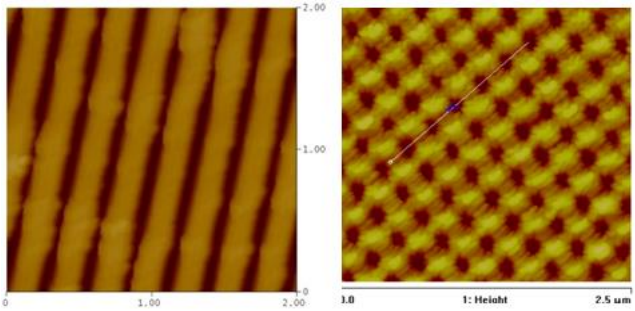

Fig. 4. AFM image of 200nm periodic (a) grating pattern and (b) hole pattern after Au deposition.

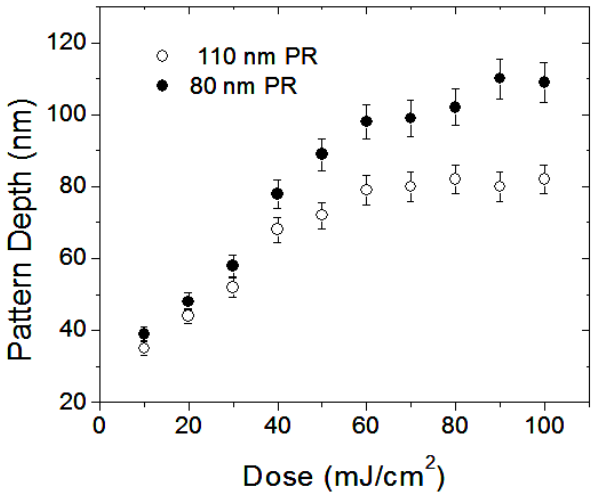

Fig. 5. The depth of the grating pattern as a function of dose after exposure to 80 nm and 110 nm PR on ARC layer.

Far-field measurements are useful in identifying the plasmon modes and their dependence on structural parameters. However, near-fields which are important in spectroscopic techniques that rely on field enhancement are more difficult to measure. Therefore we performed Finite Difference Time Domain (FDTD) simulations of the fabricated structures to estimate the field-enhancement factors in terms of transmission. The effects of the substrate were neglected in the calculations. The intensity distribution at 520 nm and 640 nm wavelength shows in **Fig. 6**(a), in an example of a gap width of 100 nm where the field is strongly enhanced in the slit, especially in a narrow region close to the sidewalls as calculated before for straight slits [**17**]. The enhancement found in the middle of the gap at the narrowest point is plotted as a function of wavelength in **Fig. 6**(b). It has been found that two resonance peaks at 520 nm and 640 nm are observed corresponding to plasmon modes of Au slit arrays. The transmission spectra were taken using the UV-Vis spectrometer and comparing the result with the simulated one. We have observed that the simulation shows less intensity as compared to the experimental value. This is because; we have not considered the substrate in case of calculation. Field-intensity enhancement factors greater than 40 are found. This factor rapidly goes up to values that exceed 100 for smaller gaps values (not shown here). This provides us the idea of high transmission of the Au grating in the visible range. Strong field enhancements in the Au gratings are very useful as surface enhanced Raman spectroscopy (SERS) substrates and also for bio-sensor application. Another similar study for nano dot patterns are in progress.

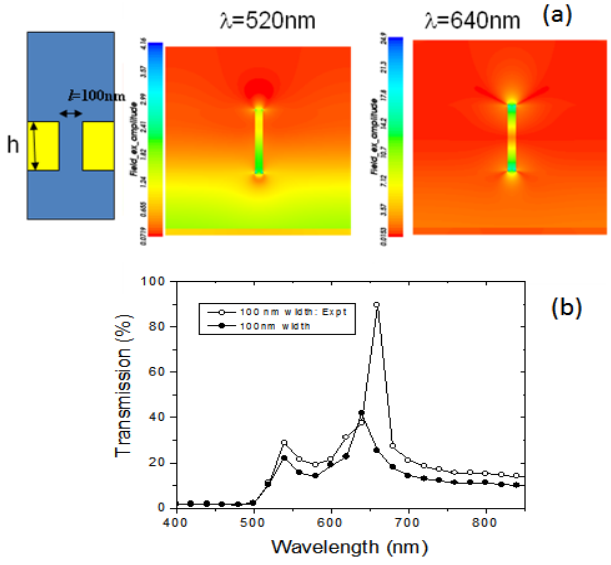

Fig. 6. (a) The schematic of the cross-sectional view of a slit array of 200 nm periodicity and corresponding FDTD simulation of e-field amplitude distribution at 520 nm and 640 nm (b) comparison of enhancement factor measured near the narrowest point of the slit from FDTD and experimental transmission spectra of the fabricated slit arrays.

Conclusion

We have developed a robust method for fabricating arrays of Au slits and holes and dot patterns on both Si and SiO_2 substrates. The PR layer thickness and process flow for removal of ARC and Cr layer are very crucial to obtain good quality periodic nano-pattern. The dose of the laser beam can be tuned to obtain high aspect ratio grating structures. Such closely packed nano patterned arrays are very useful for plasmonics, far-filed and near field enhancement studied. We have observed 40% high field enhancement in case of 200 nm period Au grating structures. Two resonance peaks are observed at 520 and 640 nm attributed to surface plasmon modes of Au slit arrays. These kinds of nano patterns are very much useful for SERS studies and sensing measurements. This potentially very interesting system requires more research both on experimental and theoretical fronts.

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