Thermal and optical nanolithography using a scanning near-field optical microscopy

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The combination between very high resolution and very high photosensitivity materials to AFM, while function as a near field optical source or as a nano-heater source, can be developed to a nanolithography tool. Although we are dealing with a serial process, the advantages of this is clear from a cost effective point of view, the simplicity, the ability to fabricate periodic and non periodic structures on a flat and non flat substrates as well as the ability of almost achieving a real time lithography process. All of these make this worthwhile in some applications. The transformation of regular commercial AFM from the microscope mode to a nanolithography tool can be easily accomplished by replacing the regular force probe with a pulled and bent fibre probe which has, at it's edge, a sub-wavelength aperture. The light emanating from a sub-wavelength aperture is initially confined to the diameter of the aperture and this size determines the nanolithography process resolution. Using these tips, the standard atomic force microscope feedback mechanism regulates the distance between the tip and the sample in the non-contact mode. The key to success with the nanolithography process is in the choice of very high photosensitive materials. In our research we are able to mention different compounds of chalcogenide film, which, in addition to the very high photosensitivity have some other unique characteristics that make them suitable for nanolithography: they are able to serve as either a positive or a negative photoresist and the fabrication of a final optical element, with very high resolution, is achieved directly after writing. Using these films a completely etched grating, with a 100 nm line width, was fabricated with an open end tip of 120 nm outer diameter. In another type of film, new organic photoresist film, based on naphthoquinone, enabled the development of 'real time' dry process nano-lithography. Because these materials are sensitive, both to light and heat, by their use the exposure can be performed, either by the optical near field or nano-thermal effect, to achieve positive or negative lithography, depending on the exposure source. Sub-wavelength gratings fabricated using this system achieved a line width down to 31 nm.

Keywords: Nanolithography; AFM; SNOM.

1. Near field nanolithography using AFM

A number of near field patterning techniques have been explored recently to extend the resolution of optical lithography beyond the conventional diffraction limits. Improved performance of the lithographic process is the key to the ongoing miniaturization of electronic and optical devices. Among the main nanolithographic methods in use, we can mention interference lithography [1], evanescent interferometric lithography [2] near field optical lithography [3] near field imprint lithography [4] and near-field two photon nanolithography [5]. The lithographic methods that are based on interference are mainly used for the fabrication of periodic structures, while serial methods are, in general, unrestricted by this constraint and can also be used for non periodic structures.

Extensive research has been reported on the use of scanning atomic force microscopy (AFM) for the fabrication of nanometre scale devices. The principle of this technique is the replacement of the regular pyramid tip, normally used for surface force sensing, with a "system" designed to deliver the required optical energy, in a very controlled manner to the surface, during the exposure stage of the lithographic process.

The advantage of using an AFM for direct writing, beyond considerations of simplicity and cost effectiveness, is that it is a mask-less process compared to other near field methods, it can be applied to fabricate periodic and non periodic structures on flat and non flat substrates and it enables the achievement of an almost real time lithography process that makes some applications worthwhile.

Different methods of utilizing this concept are mentioned in previous reports each having its own limitations. Work in this area has been published based on the following phenomena: mechanical friction [6–8], localized oxidation [7–11], localized current injection [12–14], pulsed or continuous voltage techniques [15,16], and conducting probe methods [17]. The use of AFM high precision mechanics and electronics for direct nano-scale photolithography [18–21] with normal photoresist has also been reported. Applying the concept of AFM cantilever acts as an optical source, we can mention the work that has been done [18] with a solid immersion lens (SIL) mounted on AFM cantilever and scanned while in contact with the photoresist, resulting in a line-width of 190 nm. This result was achieved due to the geometrical shape and the high index of the lens, n=2.2, which reduces the effective wavelength of the light illuminating the recording layer, thus reducing the spot size. The main advantage of this method is that the scan rate can be increased up to 1 cm/sec. The enhanced speed is a result of the high optical efficiency (about 10⁷) of the SIL. This is several orders of magnitude faster than typical reports of near-field lithography using tapered optical fibres.
In this report we will focus on, and utilize, the method of using the AFM to position a tapered optical fibre or a micropipette, which acts as a near-field optical source, to within a few nanometers of the surface of photosensitive materials as shown in Figure 1.

In this manner the illuminating beam profile remains constant and approximately equal to the aperture of the source. This system enables direct nano writing onto the photoresist or other sensitive materials with a nanometric resolution. The main drawback of this method is the slow scanning speed (less than 100 µm/sec), which is due to the low level of energy which is delivered by the fibre.

Our initial intention was to go beyond this limitation by applying these methods with the development of both a suitable nanolithography instrument with an improved energy transfer to the resist, as well as using new appropriate materials characterized by high sensitivity, large exposure dynamic range and high resolution, with the option of a developed dry thermal process, instead of a wet lithographic, process. It appears that, a nano-lithographic process based on a nano-heater source (instead of an optical source) with the combination of the appropriate materials, developed into a real time nano-lithographic process. This ability can be a significant drive towards the fabrication of nano-scale devices based on near-field lithography.

2. Experimental nanolithography set up and probe design.

The transformation of regular commercial AFM from microscope mode to a nanolithography tool can be done easily by replacing the regular force probe with a pulled and bent fibre probe that has at its edge a sub-wavelength aperture, the light emanating from a sub-wavelength aperture is initially confined to the diameter of the aperture and this size determines the nanolithography resolution process. The energy transfer to the resist is governed by the geometrical shape of the tip; hence this element is crucial to the nanolithographic process.

An experimental study, to optimize the geometrical shape of the bend-tapered fibre, was preformed in order to ensure that the maximum amount of light would emerge from the tip end. The study traces the optical power loss in the fibre. The optical fibre can be divided into five optical waveguide sections, as shown in Figure 2:

1. A straight waveguide - In this section the optical power transmission is approximately the same as a regular straight waveguide. Apart from the coupling loss, all other losses can be ignored.
2. The bend radius R - Most of the optical power loss occurs in this area and it is due to the bend radius and the defect areas caused by the bending process. The light transmission of this section can be significantly improved by an optimized R parameter.
3. Cone waveguide area - In this metal covered section (angle 100-150), the border between the core and the cladding is not fully clear. The diameter of this area begins at 20µm and its length is around 100µm. This area melts during the bending stage so that the waveguide can be approximately described as a glass core with a metal conductive envelope. In this area only the fundamental TE optical mode exists, assuming perfect conductivity of the metal coated tip. The fundamental TE mode cutoff term is: $r/λ ≤ r_{cutoff}/λ ≈ 1.841/(2πn)$ where $λ$ is the wavelength (in our case $λ=488$ nm), $r$ is the core radius and $n$ is the index of refraction. The optical LP01 mode in the single mode fibre is mainly coupled with the fundamental TE mode of the conical waveguide. In the region below $r_{cutoff}$ all the modes, except the fundamental TE mode, are either refracted or absorbed and considered as heat which diffuses to the coated tip area [22].
4. The cone waveguide section is divided into two parts, the first part is a tapered cone waveguide with a dimension larger than the wavelength, and the second part, up to the NSOM (Near filed Scanning Optical Microscope) aperture, is a tapered cone waveguide with a dimension less than ~0.5λ. In this section the optical power decreases exponentially with the distance [23]. The overall distance of this two tapered cone waveguide is ~100 nm.
5. NSOM aperture area - The aperture is smaller than the optical wavelength launch into the fibre and the final dimension of the aperture will determine the system resolution. There is a reciprocal relationship between the resolution and the power intensity that is delivered to the resist given by: $I ≈ a^6/λ^4$ where $a$, is the aperture radius [24].

Optimization of the fibre performance was achieved through the control of three parameters: R - the bend radius, Θ - the angle and L - the length of an adiabatic tip waveguide. Figures 2(a) and Figure 2(b), show fibre tips without the metal coating. Figure 2(a) shows the light loss in the bent area of an un-optimized fibre tip. The five-waveguide sections...
are marked and one can track the light scattering along the fibre tip from before the waveguide cut off area until the end tip. The light guiding can be seen by controlling these geometrical parameters, as shown in Figure 2(b), which shows an optimized transmission end tip. The optical and the thermal probe design follow the same guidelines. The only difference being, the thermal tip in section five is coated with metal in order to absorb the light and convert it to heat. Maximized radiation delivery to the tip is desirable for both processes.

![Figure 2: Fibre tips without the metal coating. a) An un-optimized tip with its five-waveguide sections. The light is lost in the bent area of an un-optimized fibre tip. b) Optimized transmission end tip.](image)

The nano-lithographic system described in this work uses an AFM (Topometrix, Santa Clara, USA) with a specially modified optical probe in non-contact mode. A CW Ar+ Ion laser (488 nm) coupled to a single-mode optical fibre was used as the light source. The output of this fibre is coupled to a bent and tapered Cr/Al coated quartz fibre tip (Nanonics, Jerusalem, Israel), which replaces the regular scanning force probe of the AFM (Figure 1). This tip consists of a single-mode elongated quartz fibre (core diameter 3.7 µm) with a 0.13 numerical aperture. The fibre is pulled in a Sutter Instruments P-2000 CO2 laser powered micropipette puller. Passing the fibre rapidly through the focal spot of a second CO2 laser, sharp, accurate, and very reproducible bends less then 50 µm from the tip are obtained. Varying the time the tip is in the beam controls the bend angle. The fibre tip is glued to a small stub, leaving a free cantilever length of between 100µm and 400µm. The precise cantilever length can be controlled to obtain a force constant K, from 0.1 N/m to 10N/m for contact mode, and tip resonance frequency in the range of 180 kHz to 380 kHz. The K values can be varied from 10N/m to 100 N/m for non-contact methods. The bent glass elements are then coated at tens of microns from the sub-wavelength aperture that is left uncoated, in order to function as a near-field optical source. This is done by shadow evaporation during rotation using a specific holder with an angle of 30°–60°, equal to the bent angle of the fibre. The probe is held a few nanometres above the sample in order to be in the near-field mode. Calculations indicate [25] that light emanating from a sub-wavelength aperture is initially confined to the diameter of the aperture and has, in the near field, an exponentially decreasing intensity distribution as the beam spreads out from the surface of the aperture. The standard atomic force microscopy feedback mechanism regulates the distance between the tip and sample in the non-contact mode. The sample is then raster scanned to create the desired pattern. The non-contact mode was chosen for the following reasons: firstly not to damage the tip because of tip–material interaction, and secondly to ensure that the patterning results are due to the lithography process and not caused by a mechanical scratching of the photoresist. The non-contact mode enforces the tip to be within a constant distance from the surface in contrast to the tapping mode where the tip is brought into a contact and jog over the surface.


Chalcogenide glasses have attracted much interest for high speed optical communication due to the advantages of excellent transparency in the mid-IR, weak non-irradiative relaxation when doped with rare earth elements for fibre amplification [26], non-linear optical properties for fast all optical switching and processing and photo induced effects [27]. Work has also been done on waveguides writing [28], fibre gratings [29], and Bragg gratings [30]. The ability of reaching high resolution can contribute to further developments in these applications. In addition, thin films of chalcogenide glass (of AsS and AsSe type) have been used as inorganic photoresist for fabrication of the final IR micro-optical element, unlike conventional photoresist techniques [31–34]. Depending on the developer composition, these photoresist may function as either positive or negative photoresist. Their high resolution, among other features, makes them particularly suitable for nano-lithography experiments.

The novelty of the nano-lithography system, described in this work, is the combination of the AFM with a chalcogenide film that can serve as a positive or a negative photoresist to fabricate a final optical element with a very high resolution directly after writing (by eliminating the need of etching processes). The present work should be distinguished from earlier work in which one line of 100 nm was written on a chalcogenide substrate using the photo-darkening effect [35]. This effect has a different mechanism to the mechanism of photo induced change of dissolution in
some solvents, which is the basis of photolithography. The photo-darkening effect, in which no material is physically removed from the substrate, is in fact a limiting factor in the lithography process, since the photo-darkened material prevents further exposure to the base. In the present work, a completely etched grating was fabricated directly onto the photosensitive with nano-metric resolution, involving the complete lithography process including exposure, development and fixing and the result serves as the final element. The reflection coefficient of the grating (amplitude and phase) can be controlled by the appropriate choice of the etched depths.

In this work As$_2$S$_3$ films were used as the photoresist material. Its composition was selected for its high sensitivity at low exposures, required due to the low light throughput of the near-field tip, sensitivity to the Ar$^+$ laser radiation (488 nm) and the requirement of being used as a positive resist, (only positive photoresist can be used in our case). The film was fabricated by vacuum evaporation of crushed chalcogenide As$_2$S$_3$ glass using a resistive evaporator. The grating, shown in Figure 3, was created on a chalcogenide photoresist film having an initial thickness of 0.1 µm based on mass evaporation measurements, with roughness of 2–4nm according to interferometer microscope measurements. A fibre tip, with an open end of 120nm outer diameter, served as the near-field optical source. The working parameters of the AFM system were: non-contact mode, relative set point 5.4 nA (50% of the free range), resonance frequency 176 kHz, scan rate 7 µm/sec. The scan area was 20x20 µm$^2$. After exposure the film was wet developed using monomethylamine (40 % solution in water) as the developer and then characterized with the same tip. Monomethylamine is the positive developer for As$_2$S$_3$ film; it dissolves the irradiated areas of the film much faster than the non-irradiated parts. Such a positive developer must be used in cases that demand high resolution photolithography.

![Figure 3: Cross-section measurement of the periodic grating.](image)

Analysis of a cross section of the grating is shown in Figure 4(a). It can be seen that the grating profile is uniform, with a dimension of 100nm (half width). The etched depth (peak to valley) is about 23nm. The As$_2$S$_3$ roughness remains the same as that of the initial film and was not affected by the development process. Since the photoresist roughness is 30–50 times smaller than the resolution of the fabricated grating, this parameter is not a limitation at these levels of resolution. Periodic sub-wavelength gratings can be fabricated by an interference method as well. In order to further demonstrate the power of the method, another grating with a varying period, consisting of two periods, 100nm and 200nm, was fabricated and is shown in Figure 4(b). The photoresist and exposure parameters were similar to those described above. The etched depth in this grating is approximately 30–32nm. The different line width results were achieved by modifying the scan procedure. To produce the 100 nm features, the shutter controlling the light transmission to the fiber was closed for each scan during the return of the tip. The 200nm feature was obtained by leaving the shutter open for the return of the tip. The profile flatness top or bottom appears to be affected by issues such as the tip light transfer and photoresist interaction, the angle and the bluntness of the tip and to imaging conditions which are also dependant on the tip.

AFM nano-photolithography has the potential to find different applications in the near future, especially when taking into consideration prospects of a significant increase of photosensitivity of chalcogenide photoresists when exposed by intense short light pulses excitation [36,37].

Nanolithography using new organic photoresist films based on naphthoquinone has also been developed. The naphthoquinone photoresist are selected and developed to match the Ar+ ion laser wavelength and the low energy output of the near-field optical source [38,39]. The photosensitive and the heat sensitive properties of naphthoquinone compounds made them a natural choice for use as a photoresist and enables the development of both regular wet photo lithography and dry process lithography. The interaction of visible light with organic solutions of 2-arylamino-3-cycloalkylaminonaphthoquinones-1,4 causes the compounds to form ring structure derivatives of the naphthimidazoles [39]. A study of the thermal stability of the solid phase of these types of naphthoquinones has shown that they are chemically stable below ~100°C. However, in air they sublimate directly at melting point (~100°C), and in a vacuum at lower temperatures [40]. On the other hand, the isomer created by exposure to light is stable at higher temperatures (~115°C). Hence, appropriate optical treatment enables the separation of the two phases. The separation between the two phases being dependent on the naphthoquinone compounds.

These two features, photosensitivity and stability up to the sublimation point, suggests the use of naphthoquinones as a photoresist [41], which are developed after exposure by sublimation. Since the illuminated phase has a higher thermal stability, it will act as a negative photoresist. Alternatively, by inscribing a pattern thermally, the film will act as a positive resist without requiring further development. These two methods of inscribing a pattern allow for totally dry processes that eliminate certain steps, as compared to classical optical photolithography, and are effective in terms of total cost and time. Thermal inscription also allows real time lithography. Real time lithography may enable the development of new manufacturing nanotechnological capabilities.

Figure 5 shows the absorption curve of the 2-cyclohexylamino-3-piperidinonaphthoquinone-1,4 used as a photoresist. The absorption peak of close to 488 nm can be observed. This material sublimates in air at a relatively low temperature (~100°C). The melting point of the remaining solid phase occurs at 115°C. Resist films of this compound were used in subsequent experiments. The thickness of the resist films was approximately 0.12 μm. The photoresist films were prepared by vacuum thermal evaporation at about 120°C and 4•10⁻⁶ Torr. The glass roughness was 1 nm according to interferometer microscope measurement and the film roughness was about 2-5nm according to an AFM measurements. Fibre tips with open ends of 70-100nm outer
diameters served as the near field optical source. The nanolithography system used is the same as described in the previous section. The working parameters of the AFM system for near field lithography were: a non contact mode, a relative set point 40%-50% of the free range, a resonance frequency of 24 kHz and a scan rate of 3 µm/sec. The lower resonance frequencies of the tip are preferable since they give better feedback signals, and enable a more stable lithographic exposure process. The scanned areas were 4x4µm. After exposure, a developing and fixation thermal treatment was performed and the film was brought back to the AFM for measurement and characterization with the same tip- now without launching any light into the fibre.

The lithographic results are shown in Figure 6. The measurement of a 57nm full width half maximum (FWHM) line width can be seen (Y diff in the figure) with an approximate etched depth of 80nm, giving a 5:7 aspect ratio. The photoresist behaves, as expected, as a negative one, where the non-exposed photoresist disappears during the development process performed by thermal treatment. This is visualized by the fact that the bottom of the grating is at the same level as the substrate where the non-exposed photoresist has been removed by the developing process.

Because this material sublimates in air at low temperatures (~100°C) and the remaining solid phase melts at ~115°C, a pattern can be inscribed by means of a localized nano heating source. By utilizing the same geometry of the fibre tip, but this time with a metal-coated blocked end tip, the previous near field optical exposure source converted to a nano-heating source. The requirement that has to be fulfilled is that the localized temperature at the edge has to be above the sublimation temperature of the exposed phase (115°C). The heat source is the light, transferred into heat, by utilizing the conductivity of the metal that covers the tip, and causes local heating and evaporation of the “exposed” material. This approach eliminates the thermal developing required when the film is optically inscribed. It also eliminates the need to remove the sample, after exposure, from the system in order to obtain the structure of the film. This procedure will enable the achievement of a “real time” nano lithographic process. This may open new horizons in nanotechnological manufacturing. In addition, the introduction of a controlled external source to heat the fibre ends, could create a continuous lithographic process.

In the following set of experiments aimed at achieving thermal lithography, the same material that is used for optical lithography (2-cyclohexylamino-3-piperidinonaphthoquinone-1,4) with similar layer thicknesses was used. This time a blocked, metal-coated tip, with an outer diameter of 50-70nm, was used. The assumption was that no light escapes, but only heats the edge of the tip. Heating the metal coating is not, however, solely confined to the immediate tip vicinity. The sensitivity of the thermo-chemical lithographic process therefore strongly depends on the tip induced thermal field enhancement caused by its shape and coating irregularities. The AFM system parameters were: a non contact mode, a relative set point 40%-50% of the free range, a resonance frequency of 32 kHz and a scan rate of 7µm/sec. After heat exposure the film was characterized with the same tip.

Analysis of a cross section of the grating is shown in Figure 4. Measurement of the 31nm line width (FWHM) can be seen (Y diff), with the approximate etched depth of 90nm, giving approximately a 3:9 aspect ratio. Although the physics governing the process still needs to be elucidated, one can clearly see that the pattern obtained is that of a positive resist. This is apparent from the fact that the top of the grating is at the same level as the original level of the photoresist and the process of exposure caused the removal of the photoresist. Therefore, using the same material under different exposure conditions, one can obtain a positive or negative pattern in the resist with a very high nano-scale resolution.

Figure 6: Sub-wavelength grating made with optical near field exposure on 2-cyclohexylamino-3-piperidinonaphthoquinone-1,4.
By using the same material, under different exposure conditions, we obtain either positive or negative nanolithography. Negative lithography is achieved using optical near field exposure, and positive lithography is achieved using a localized thermal nanoheating source. Based on thermal lithography, a “real time” dry process nanolithography was developed. These two methods can be applied for the creation of a variety of patterns, periodic or non-periodic, that demand nano-scale resolution.

To summarize, the concept of a commercial AFM that transfers to a nanolithography tool is demonstrated. Results of the development of wet nano-photolithography process based on chalcogenide were shown. Results of the development of a dry optical nano-photolithography process and a dry thermal nanolithography, based on naphthoquinone films, was also demonstrated. Both materials enable positive and negative nanolithography, while in the chalcogenide it depends on the developer type, after near-field optical exposure in the naphthoquinone, which depends on the exposure mechanism, the negative lithography achieved by near field optical exposure and the positive lithography achieved by thermal nanolithography exposure that also has the benefit of a real time process. The combination of dry process lithography with a real time process can be very significant in the field of nanolithography fabrication capabilities.

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References

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**Figure 7**: Cross section of sub-wavelength grating made with a localized thermal exposure on 2-cyclohexylamino-3-piperidinonaphthoquinone-1,4.