Scanning near-field photolithography—surface photochemistry with nanoscale spatial resolution

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This *tutorial review* describes recent advances that have challenged the traditional view that the Rayleigh limit, of approximately $\lambda/2$, represents the ultimate resolution accessible using optical methods. Near-field optical methods offer a powerful capability for optical measurement and manipulation of materials. Using a scanning near-field optical microscope coupled to a UV laser it is possible to create photopatterned molecular structures with dimensions nearly 15 times smaller than the Rayleigh limit. Near-field methods offer the possibility for selective initiation of surface chemical transformations with exquisite spatial resolution, bringing the prospect of unifying top-down and bottom-up nanofabrication into view.

Introduction

The integration of top-down (lithographic) and bottom-up (synthetic) fabrication remains one of the outstanding challenges in nanoscale science and technology. While sub-10 nm inorganic structures may be fabricated by electron beam lithography, the state-of-the-art is significantly less advanced in molecular nanotechnology. There is a critical length regime, smaller than 100 nm but larger than the dimensions of a single molecule, in which there are currently no established tools for executing specific chemical transformations. What is required is a methodology with a resolution similar to that of a single macromolecule, but the capacity to initiate chemical synthesis. In this article I shall attempt to show that approaches based upon the use of near-field optical methods may provide exactly this capability. While scanning near-field optical microscopy (SNOM) is regarded as a rather challenging method, SNOM apparatus can be used surprisingly straightforwardly to perform lithography, bringing all of the synthetic flexibility and versatility of photochemical methods within reach of the chemist at a spatial resolution significantly beyond the limits of conventional photochemical methods.

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Optical microscopy and lithography

There are many reasons why optical approaches are attractive although instinctively one may, perhaps, not immediately regard them as being within the remit of nanotechnology. Optical microscopes are among the oldest scientific instruments, and while their versatility, simplicity and ease of use has made them ubiquitous in biology laboratories, textbooks lead us to believe that optical microscopy is strictly a microscale characterisation tool. Traditionally, the limit of optical microscopy has been thought to be represented by the Rayleigh limit:

$$\text{Resolving power} = \frac{0.61\lambda}{n \sin \alpha} \tag{1}$$

where λ is the wavelength of the light used and $n\sin\alpha$ is the numerical aperture. Practically speaking, this may be regarded as approximately $\lambda/2$. However, recently there have been exciting advances in the development of new approaches to optical characterisation that have enabled this limit to be significantly exceeded. These include near-field methods (the main focus of this article) but also a number of new far-field methods. One illustration is stimulated emission depletion microscopy (STED)[1] in which a diffraction-limited excitation beam (*i.e.* a beam focused as much as the Rayleigh criterion allows) overlaps a doughnut-shaped beam that is capable of de-exciting fluorophores by stimulated emission. Using this approach, a resolution over an order of magnitude better than that defined in eqn (1) has been reported. It is clear that the Rayleigh limit is not, after all, the last word on optical resolving power.

Optical lithography remains the mainstay of the semiconductor device manufacturing industry. In conventional photolithography, light is passed through a mask, interacting with a film of photoresist deposited onto a wafer surface leading either to the cross-linking of a photosensitive molecule, or the photodegradation of a macromolecule, resulting in the formation of a pattern after development of the resist. To make smaller features, it is necessary to reduce the dimensions of the features in the mask. However, this cannot be done arbitrarily: Rayleigh's criterion again sets a lower limit to the dimensions of the features in the mask. While first generation photo-resists used visible light, electronic engineers and materials scientists have been extremely creative in pushing the limits of photolithography. The primary weapon in this drive has been a reduction in the wavelength used; while this sounds trivial, for current commercial chips, with gate lengths of *ca*. 100 nm, the design of suitable resist materials (ones in which useful chemistry is excited with high efficiency at small wavelengths) has been a significant challenge. Currently, there is much interest in 193 nm lithography but work is already in progress on the development of extreme UV lithography, which will use wavelengths in the range 10–50 nm; traditional organic molecular chromophores do not absorb strongly at these wavelengths.

Near-field optical methods

When an aperture is illuminated, light propagates through the aperture. This propagating excitation may be detected at a distant point and is subject to diffraction. However, at locations close to the aperture, evanescent electric fields (near fields) give rise to optical excitations that are not subject to diffraction effects. The near field excitation received little attention for many years, because of the experimental difficulties associated with its detection. However, it was realised early in the twentieth century by Synge that near field exposure could be utilised to carry out non-diffraction-limited optical characterisation of samples.[2] The key requirement was to hold the specimen very close to the aperture. Synge's very simple solution was to form a nanoscopic aperture in a screen and to translate the screen across the sample. Provided the separation between the screen and the sample could be maintained as a very small distance, it would be possible to confine the optical illumination and acquire optical images with a resolution significantly superior to the Rayleigh limit (Fig. 1). In principle, such an approach could be applied to photolithography, too: by maintaining the mask only a few nm from the resist layer, it should be possible to expose the resist in the near-field and evade the Rayleigh limit. However, both approaches are subject to an enormous practical limitation: the maintenance of a screen at nm separations from a surface across a significant distance is extremely difficult. A small dust particle or surface imperfection would be sufficient to create a large enough gap between the sample and the mask or screen to significantly degrade resolution and, probably, cause diffraction effects.

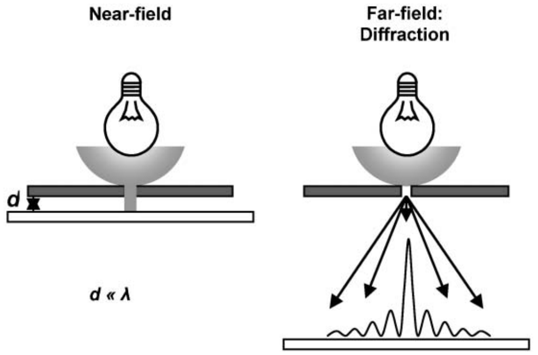


Fig. 1 Provided a sample is held close enough to a nanoscopic aperture, light may interact non-diffractively with it.

A solution to these practical challenges was found in the 1980s in the form of the scanning near-field optical microscope (SNOM), also known as the near-field scanning optical microscope (NSOM), embodied in the paper by Betzig and Trautman in 1992[3] in the form most commonly used at present, based on shear-force feedback. The key to the success of the SNOM in realising, after six decades, Synge's simple concept was that the screen (*i.e*. an object with a very large area) was replaced by a tip. The probe was an optical fibre, formed into an asperity with a nanoscopic aperture (*ca*. 50 nm) at its apex. In this way, only the aperture needed to be scanned—the confinement of light by the optical fibre obviated the requirement for a screen. The fibre may be made of glass or silica, etched in HF or heated in a laser and pulled to yield a sharp tip, and must be coated with a metal (usually Al but sometimes other metals such as gold) to prevent leakage of the electric field laterally through the probe. In the shear-force feedback system, the optical fibre is attached to one leg of a tuning fork, attached to a circuit that drives its oscillation and also measures the feedback signal. The type of tuning fork employed is also commonly used in digital watches to keep time, and is a miniaturised version of the device familiar to musicians. As the probe interacts with the sample, the oscillation is damped (as a result of shear forces) and this effect may be detected and fed into the control electronics to adjust the height of the probe (using a piezoelectric scanner). The arrangement is illustrated schematically in Fig. 2. There are two other principal types of SNOM probe that utilise

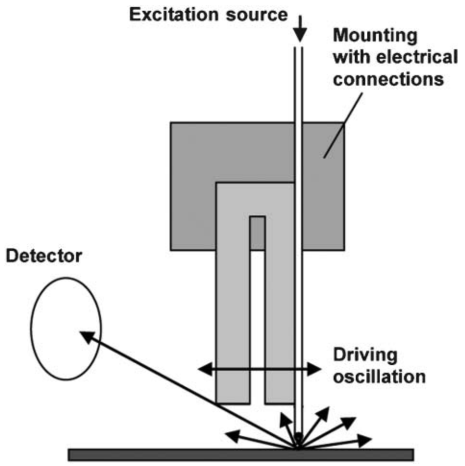


Fig. 2 Schematic illustration showing the operation of a shear-force detection SNOM system.

optical apertures. One is based upon a bent optical fibre, doubling up as a lever the deflection of which can be measured optically. The other employs an atomic force microscope (AFM) style cantilever probe, in which the pyramidal tip is hollow and has a small aperture at its apex. These are both effective, but the shear-force system is the more common.

Scanning near-field optical microscopy

With the advent of SNOM there was a great deal of excitement. While scanning probe microscopy (SPM) had already made a major impact on surface science by the early 1990s, particularly through the scanning tunnelling microscope (STM) and the AFM, there were unique benefits to an optical probe with genuinely nanometre scale resolution. In biology, for example, an optical nanoprobe could, in principle, exploit the many labelling methods developed by microscopists—but with much superior resolution. In chemistry, an appealing feature of SNOM is the potential offered for spectroscopic investigation. While STM offers the capability to carry out scanning tunnelling spectroscopy, the data acquired are nevertheless rather different, and do not provide the sort of information on composition and bonding associated with conventional spectroscopic techniques. Early on it was demonstrated that Raman spectra could be acquired using a SNOM probe, for example, and many tantalising glimpses were provided of the possibilities that the technique offered. For a detailed review of these and other applications of SNOM, the reader is referred to Dunn's excellent article.[4]

However, despite such enormous potential, and widespread excitement, SNOM has unfortunately largely failed to realise its potential as a nanoscale *characterisation* tool. Impressive data have been acquired by SNOM, and a strong community of users continues to exploit the technique. They have developed ingenious techniques that have provided unique insights into the optical properties of nanostructures. However, SNOM has failed to have the widespread impact that was at one time anticipated. There are a variety of reasons for this. Perhaps the most significant obstacle has been a general perception that SNOM is a difficult technique. There is, perhaps, some justification for this. For example, when illuminating a sample through an optical probe as illustrated schematically in Fig. 2, most of the light emitted from the sample (for example, through the excitation of fluorescence in a biological specimen) is lost, being scattered in all directions while the detector occupies a fixed location in space. Alternatively, if the signal is collected through the probe, the problem is that the amount of light collected is modest and may be reduced by losses in the fibre. Given advances in other techniques, and the fact that a good confocal microscope can achieve a resolution of 200 nm—hard to better by SNOM in studies of difficult systems—SNOM has failed to become widely used.

Fortunately, as will be described below, most of the difficulties associated with SNOM evaporate when the instrument is used to carry out *lithography*. In fact, optical fibre-based SNOM probes really are very effective tools for the selective illumination of nanoscopic regions of materials, and shear-force feedback systems are convenient to use and reliable. Once the requirement to acquire a signal is removed, a SNOM becomes a very much easier instrument to work with!

Apertureless SNOM

In addition to methods based upon optical aperture probes, it is also possible to excite near-field phenomena in the absence of an aperture by using a metal tip as the probe. There has recently been a growth of interest in these so-called apertureless SNOM techniques, in the hope of delivering superior resolution to that provided by aperture probes. They rely upon the fact that when a nanoscale metallic asperity is held in close proximity to a surface and illuminated with polarised light, the electric field associated with the excitation may be significantly enhanced in a small region directly beneath the tip.[5] The magnitude of the enhancement in the field strength may be very large—several orders of magnitude under optimal conditions. The phenomenon has become known rather evocatively as "the lightning-rod effect". The field enhancement is associated with scattering from the tip, and consists mainly of non-propagating (evanescent) components. The advantages of apertureless approaches are that they deliver significantly enhanced resolution compared to techniques based on aperture probes and, moreover, tips are significantly easier to fabricate than optical fibre probes. Fig. 3 shows the extent of the resolution improvement that is possible in principle by comparing the spatial variation in the electric field

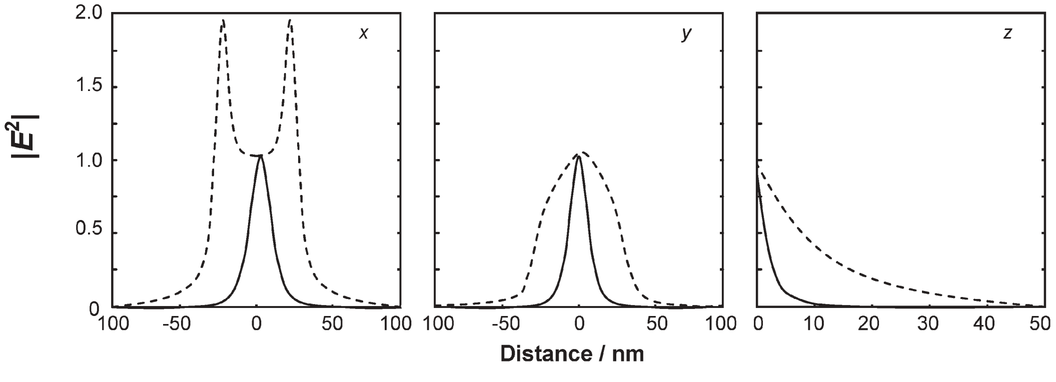


Fig. 3 Decay of the electric field intensity $|E^2|$ along the x, y and z directions (z is parallel to the probe axis) for an aperture probe (dashed line) and a silver plasmon probe excited aperturelessly (solid line). (Reproduced with permission from ref. 5. Copyright 1995 Elsevier.)

strength associated with a conventional aperture probe with that associated with a plasmon excited aperturelessly from a silver probe.

Apertureless approaches offer the same attractive capability for carrying out spectroscopic characterisation of materials. Apertureless Raman microscopy has been used to carry out spectroscopic characterisation of single carbon nanotubes by Novotny and co-workers, for example.[6] In addition, a variety of more sophisticated optical measurements is possible. It has been demonstrated that the magnitude of the field enhancement under a silver asperity is sufficient to enable the excitation of non-linear optical processes. For example, two-photon absorption experiments have been reported[7] and second harmonics have been excited from metal tips.[8] Fluorescence measurements are also possible. By attaching a donor chromophore to the tip and an acceptor on the surface, for example, it is possible to carry out a kind of localised, scanning fluorescence resonant energy transfer (FRET) experiment. These capabilities are all very exciting. The best resolution achieved to date using apertureless techniques does appear to exceed significantly the achievements of aperture-based SNOM. For example, Novotny and co-workers have reported a resolution of 20 nm in their apertureless Raman studies of carbon nanotubes.[6] However, against this it must be noted that apertureless SNOM is, if anything, even more technically challenging than aperture-based measurements. It remains to be seen how widely adopted it will become, therefore.

Why use a SNOM for lithography?

It was realised soon after its initial development that an aperture-based SNOM system provides, effectively, a very small light source and, therefore, that it should be possible to carry out lithography with it. It is perhaps worth reflecting, before proceeding further, on the potential reasons for exploring SNOM-based lithography.

One potential motivation is provided by the fact that photolithography is the mainstay of semiconductor device fabrication, but that as device sizes in commercially fabricated components decrease, there will be increasing pressure to develop new lithographic processes to enable manufacturers to keep in step with the relentless, exponential progress charted by Moore's law. Extreme UV (EUV) lithography provides one solution, but the development of new resist materials, with chromophores that work at ever-decreasing wavelengths, presents a synthetic chemical challenge. The exploitation of near-field optical techniques to deliver enhanced resolution without the need to reduce the wavelength of the illumination source is clearly attractive. A drawback of any scanning probe technique is its serial nature (the probe writes only one feature at a time). However, the development of massively parallel approaches to AFM lithography (for example, the Millipede system developed by Binnig and co-workers at IBM[9]) has provided a new paradigm for probe lithography that addresses this concern, although admittedly not for near-field optical methods. In principle, therefore, near-field methods offer a route to the photolithographic manipulation of matter on nanometre length scales that may address some of the problems associated with electronic device fabrication.

Perhaps a more attractive motivation is the widespread interest in the development of methods for the organisation of molecules on nanometre length scales. Outside of the electronic device industry, there are a plethora of problems in nanoscale science that may be solved using nanostructured assemblies of molecules. These include both fundamental investigations of molecular behaviour, and much more application-driven research, for example into the development of novel types of ultra-sensitive systems for biological analysis. This interest has led to the development of a variety of scanning probe lithography systems. Three of the most widely used are illustrated in Fig. 4. For a detailed treatment of these methods, the reader is directed to the excellent review by Kramer *et al.*[10] Here we simply sketch the basic principles. In dip-pen nanolithography, an AFM probe is "inked" in a solution of a molecular adsorbate and traced across a suitable substrate. Under ambient conditions, a liquid bridge forms between the tip and the surface, facilitating transfer of molecular material. DPN has been used to create molecular patterns in a variety of ways and has realised very high spatial resolution (*ca.* 15 nm). A wide variety of "inks" have been reported. In contrast,

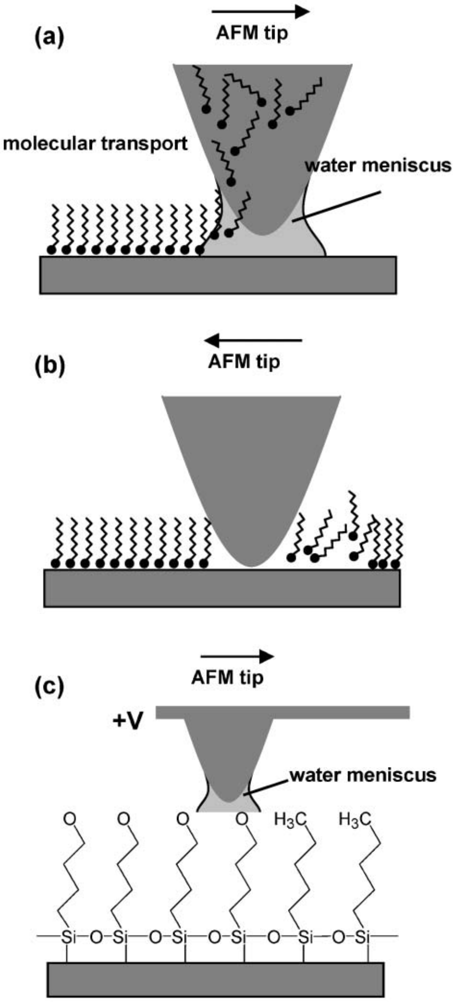


Fig. 4 Techniques for molecular nanopatterning. (a) Dip-pen nanolithography, (b) nanoshaving/nanografting and (c) local oxidation lithography.

nanoshaving/nanografting relies upon the selective *removal* of adsorbates, usually thiols. Upon clearing of the surface it may be in-filled with a second adsorbate. Impressive spatial resolution has been achieved by nanografting. However, its major limitation is its reliance upon mechanical forces for surface modification—adsorbates must be used that may be readily displaced, in a selective fashion, at loads accessible in an AFM system while maintaining a small contact area. In neither case is the selective initiation of a chemical reaction a possibility. The technique that provides the best capability in this direction is local oxidation lithography (Fig. 4 (c)), where a potential difference is applied between an AFM tip and a sample under ambient conditions. A liquid bridge again forms between tip and sample, providing a kind of one-dimensional electrochemical cell. Remarkable spatial resolution has been achieved in this way (better than 10 nm), and the apparatus required is straightforward. However, the specificity of the chemistry accessible using such an approach, in which, presumably, the driving force for bond-breaking is a locally high electric field gradient, is not expected to be very high. It is conceivable that, in principle, near-field optical methods may offer much wider synthetic versatility because of the variety of photochemical methods that has already been developed both for surface functionalisation and for organic synthesis. A good illustration is the development of light-directed solid-phase synthesis,[11] which now forms the basis of the on-chip synthesis of huge arrays of oligonucleotides used by Affymetrix to produce their Gene Chip. If such precision in surface chemistry manipulation could be made feasible with nanometre spatial resolution, then the result would be an extremely powerful tool indeed—a top-down patterning method that enabled localised chemical synthesis—that might aid significantly in spanning the divide between top-down and bottom-up fabrication. However, we must first demonstrate that near-field optical methods are useful for nanoscale patterning.

Early applications of SNOM for lithography

The first report of the use of SNOM to conduct lithography, by Betzig *et al.*,[12] was promising. Using an optical fibre probe in shear-force mode, they wrote structures into a Co/Pt multilayer film using visible light (488 and 514 nm). In regions heated near to the Curie temperature of the medium (*ca.* 300 °C), domains were formed with opposite magnetization that could subsequently be imaged using SNOM. When adequate powers (*ca.* 5 mW input power from an argon ion laser) were utilised, it was possible to write features with diameters of 60 nm. In order to optimize the process it was necessary to ensure that adequate power was passed through the probe to facilitate sample heating, while at the same time ensuring that the input power was not great enough to damage the aluminium coating on the probe.

Building on this promising start, Krausch and co-workers utilised a SNOM to expose films of conventional photoresist.[13] Their objective was to use a process already well-developed and tested in device fabrication, but to replace the conventional mask/lamp combination with a SNOM and test the resulting improvement in resolution. Using an argon ion laser (λ = 454 nm) they were able to write structures as small as $\lambda/5$ (*ca.* 80 nm) into a resist based on a phenol–formaldehyde resin which becomes base-soluble on exposure to light. The features formed in the photoresist were mechanical replicas of the intensity distribution in the optical near field of the tip. It was found that the features could be fitted with a Gaussian intensity distribution with a width of approximately 100 nm, and a height of *ca.* 15 nm. A grating was fabricated with a period of 164 nm and a line width of 82 nm. These results confirmed that using SNOM it was possible to break the diffraction limit in lithographic mode by a significant margin. A similar approach was adopted by Smolyaninov *et al*, who utilised a standard negative-tone resin-based photoresist in studies using UV light from an excimer laser (248 nm).[14] Exposure of the resist using a SNOM led to the photochemical generation of a cross-linked network that was insoluble in the developer. The resulting specimens were characterized before development, by using shear-force imaging with the same probe employed to modify the sample, and after development, by both atomic force microscopy (AFM). A non-linear dependence of the feature size on the light power was reported. Under optimal conditions, features of *ca.* 100 nm size could be written with an uncoated optical fibre.

Although these results represented excellent progress, and certainly demonstrated that sub-diffraction-limited resolution was achievable, they nevertheless left much to be desired. Given that there were high hopes for the development of a lithographic tool with extreme resolution, it was disappointing that these initial studies failed to deliver what ought to have been the ultimate resolution—matching the diameter of the optical fibre. It appears that a major problem in these early studies was the finite thickness of the resist layer—10s of nm at best. Modelling studies have shown that the electric field associated with the aperture diverges reasonably rapidly in the dielectric layer beneath the probe. Recently, this phenomenon has been studied by Riehn *et al.*[15] They patterned poly-(phenylene vinylene) (PPV) layers using a SNOM as the light source and reported a resolution of, at best, 160 nm. They modelled the behaviour using the Bethe–Bouwkamp model, and concluded that a surface of constant intensity was formed that just touched the substrate under a 40 nm precursor film and had an extent of approximately half the diameter of the feature prepared experimentally. They proposed the formation of a central core surrounded by a gel phase. The steep profile of the electric field predicted by their model indicated that the polymer at the top of the sample absorbed 20 times the dose of the polymer at the substrate. However, the region of excitation in a film of tens of nm thickness is expected to be much larger than the area directly beneath the aperture. In the work of Betzig *et al.*, there was an additional complication, because they relied upon localised heating. As a consequence, additional broadening may result from thermal migration away from the region exposed beneath the fibre aperture.

These problems were identified by Fujihara and co-workers.[16,17] Recognising the crucial role played by the thickness of the dielectric layer, they proposed addressing the problem through the use of monolayer films. They prepared Langmuir–Blodgett films of a photochromic material containing 4-octyl-4′-(5-carboxypentamethyleneoxy) azobenzene. On exposure to UV light (λ = 350 nm) this molecule undergoes a *cis–trans* conformational change. The change may be reversed by the action of heat or light. They reported a resolution of 130 nm. It is unfortunate that this does not represent an improvement on the results reported in the work described above, but the essence of their hypothesis was nevertheless correct, and the selection of appropriate monolayer resist materials is a key criterion for the realisation of the full potential offered by SNOM-based lithographic approaches, as will be discussed below.

The earliest attempts to carry out lithography by SNOM-based methods mirrored, to some extent, the frustrations encountered when doing microscopy. The literature contains a variety of examples of innovative patterning schemes that nevertheless do not quite deliver the precision that might have been hoped for. Here we simply mention a few examples. Conjugated polymers have figured prominently in the work published to date, largely because of both their technological importance and the difficulties associated with patterning them by more conventional methods. There has been significant interest in exploiting the susceptibility of conjugated polymers to photo-oxidation as a means for patterning them at the nanometre scale, using an NSOM to deliver excitation to localised regions in polymer films. For example, Wei *et al* studied thin films of (3,4-diphenyl-2,5-thienylene vinylene). They reported comparatively diffuse structures with linewidths of *ca.* 200 nm.[18] Buratto and co-workers patterned films of poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) using light from an argon ion laser coupled to an NSOM[19] but were not able to realize a superior resolution. In part, no doubt, the poor resolution in these studies was a consequence of the finite thickness of the resist. The same authors also studied the exposure of *tris*-8-hydroxyquinoline aluminium (Alq_3) films. Here there was an additional problem in that active species created by the initial exposure of the sample diffused away from the region of initial exposure. On small length scales, even small amounts of diffusion, or thermal migration, may cause a significant degradation of the resolution.

Some efforts have been made to pattern inorganic materials using SNOM-based methods. For example, Madsen and co-workers used an NSOM coupled to an argon ion laser to write oxide structures into hydrogen-passivated silicon surfaces, which were then used as resists during etching of the Si substrate with KOH.[20] The structures observed consisted of a central line with a full width at half maximum height (FWHM) of, in one case, 111 nm, and in another, 126 nm. These narrow structures were bordered by slightly wider features attributed to an interference pattern dominated by far-field excitation through the side walls of the uncoated fibre used. Narrower structures (50 nm) were observed in the absence of the optical excitation, attributed to the presence of the electrostatic potential between the probe and the amorphous Si layer. Significant improvements were produced when aluminium-coated fibres were used. The Al coating prevented far-field emission through the fibre walls, and resulted in the formation of much better-defined structures with widths not much in excess of 50 nm.[21] These structures represent some of the most clearly resolved in these early studies. Hosaka and co-workers examined a different inorganic system, amorphous GeSbTe films whose structure could be modified by localized heating by light from a pulsed diode laser, emitting at 785 nm, delivered through an NSOM probe.[22] They achieved somewhat superior resolution, demonstrating the fabrication of 60 nm structures. A variety of other approaches have been explored, some of which are more complex and use less conventional resist materials. However, there are few reports of the fabrication of structures smaller than 100 nm and many processes have yielded structures significantly larger.

Photochemistry of self-assembled monolayers

It is clear from the preceding discussion that early efforts to pattern materials using SNOM-based methods did not routinely deliver the resolution hoped for. *A priori*, it might have been expected that the resolution would be determined by the diameter of the aperture. As we will see below, significantly better resolution is, in fact, achievable. The key to unlocking the potential offered by the SNOM for lithography is to control the divergence of the electric field beneath the aperture. The best way to achieve this is to ensure that the thickness of the photoactive writing medium is minimised. The ultimate thin film is a monatomic layer. One system that presents just such a writing medium is a monolayer of alkylthiols adsorbed onto a gold surface. Alkylthiols, $HS(CH_2)_nX$, adsorb spontaneously onto gold surfaces forming dense, well-ordered monolayers (SAMs) that provide versatile templates for the construction of complex molecular architectures. On exposure to UV light in the presence of oxygen, the alkylthiolate adsorbate species is oxidised to yield an alkylsulfonate:[23]

$$\text{Au–SR} + {}^{3}/_{2}\text{O}_2 + \text{e}^- \rightarrow \text{Au} + \text{RSO}_3^-$$

The sulfonate oxidation products are, in contrast to the alkylthiolates, only weakly bound at the gold surface, and they may be displaced, either by rinsing or by immersion in a solution of a second thiol, to generate a chemical pattern. The process is illustrated in Fig. 5, where a carboxylic acid terminated thiol is photopatterned. After immersion of the sample in a solution of a methyl-terminated thiol, a chemical pattern is formed that may be imaged using a variety of methods including SEM. The advantage of depositing both chemistries in a solution-phase self-assembly process is that the entire specimen exhibits well-ordered adsorbates with relatively low defect densities.

The surface modification effected by exposure of a SAM to UV light involves a modification of the bonding in S, which is distributed with monolayer coverage on the gold substrate—a monatomically thick resist layer. In principle, therefore, these systems are ideal candidates for the testing of near-field photolithographic processes.

Before carrying out any nanolithographic experiments, it is first necessary to understand in better detail the nature of the mechanism responsible for SAM photo-oxidation, in order to establish the appropriate wavelength for the light to be coupled to the SNOM. Published work on micron-scale photopatterning of SAMs has generally used mercury arc lamp sources, which typically have broad emission spectra. A

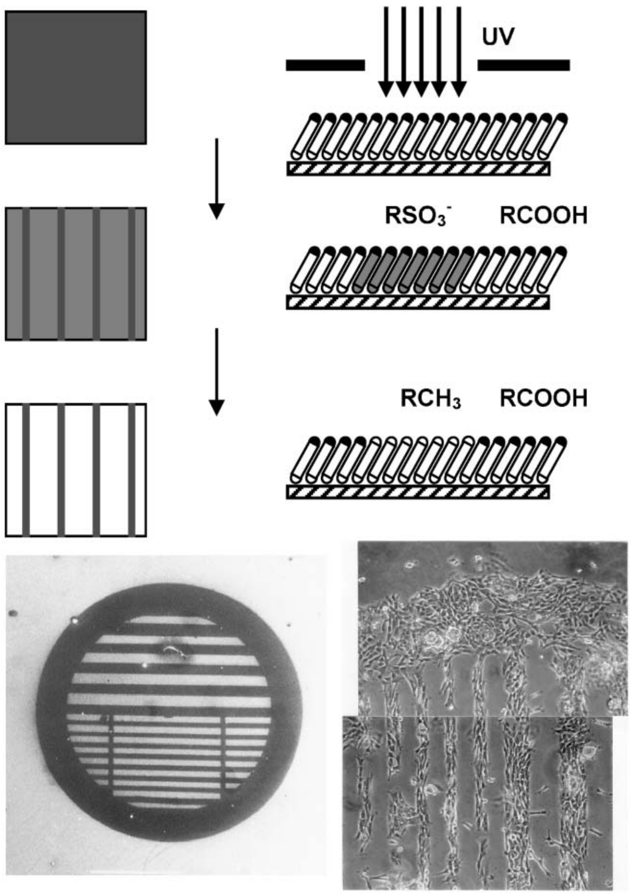


Fig. 5 Top: schematic diagram showing the photopatterning of a SAM of alkylthiolates adsorbed on a gold surface. Bottom left: SEM image showing regions of COOH-terminated thiols (dark) and CH_3-terminated thiols (bright contrast). Bottom right: optical micrograph showing murine fibroblasts cultured on a similar sample.

SNOM requires an intense, collimated light source—a laser—with a well-defined wavelength.

The mechanism of photo-oxidation has been the subject of some debate. Early reports invoked hot electron emission, singlet oxygen and even ozonolysis. While it initially attracted interest, the ozonolysis hypothesis was readily refuted. Using a lamp equipped with a filter designed to eliminate ozone formation, Brewer *et al* provided clear evidence that oxidation of SAMs could occur in the absence of ozone.[24] It was found that monolayers of carboxylic acid terminated SAMs on both gold and silver surfaces oxidized rapidly to yield alkylsulfonates when exposed to light with a wavelength of 254 nm. Recently, a more detailed kinetic study has been performed, using static SIMS to determine rates of photo-oxidation on exposure to UV light with a wavelength of 254 nm,[25] and this has provided strong evidence that the process of photo-oxidation is initiated by hot electrons formed by the interaction of UV photons with the gold substrate. Carboxylic acid terminated thiols were found to photo-oxidise rapidly compared to methyl terminated thiols of similar length. Measurements of the contact potential differences of SAMs on Au and Ag yielded data that correlated with the rate constants determined from SIMS data. In particular, it was found that the work functions of carboxylic acid terminated SAMs are larger than the energy of a 254 nm photon, while those of methyl terminated monolayers are smaller. These data may be rationalised as follows. In a carboxylic acid terminated SAM, absorption of a UV photon may lead to the promotion of an electron from the Fermi level to an excited state, but not to photoemission. These excited electrons may tunnel into an antibonding state in the adsorbate sulfur atom, leading to oxidation. In contrast, for methyl terminated SAMs, absorption of a UV photon may lead to photoemission. Photoemitted electrons will have small kinetic energies, and will most likely be scattered by the alkyl chains above the surface, but nevertheless the number of electrons available for the initiation of oxidation will be significantly reduced. The transfer of hot electrons from the Fermi level to the adsorbate sulfur thus becomes the rate-limiting step, although adsorbate order still plays a role. For example, carboxylic acid terminated thiols pack less closely on silver than on gold, and a concomitant increase was reported in the rate constants for photo-oxidation. Similarly, for both acid and methyl terminated SAMs, the rate of oxidation decreases with increasing alkyl chain length, because increasingly strong non-covalent inter-chain interactions decrease chain mobility and impede the diffusion of oxygen to the sulfur–metal bond.

The oxidative chemistry of SAMs is rather complex. Ozonolysis is not excluded in all circumstances, and for arc lamp sources, a variety of processes may occur. Significant differences were observed between the rates of oxidation under well-defined conditions (exposure to 254 nm illumination) and those measured using mercury arc lamp sources. For example, when exposed to 254 nm light, acid terminated thiols oxidize much faster than methyl terminated adsorbates—the direct opposite of the observation made earlier for an arc lamp source. This is explained by differences in the mechanisms of oxidation. The dominance of intermolecular interactions in determining the rate of oxidation during exposure to the arc lamp source suggests that gaseous reagents are important under those conditions. However, when a well-defined light source emitting at 254 nm is used, these species are absent and it is believed that hot electron formation provides the main impetus for SAM oxidation.

A final requirement before proceeding to explore SAM nanopatterning is a means of characterising any structures that might result. In Fig. 5, the patterns consist of adsorbates of similar length that differ only in the nature of the functional group located at the uppermost end of the adsorbate molecule. To characterise a nanometre scale pattern of this type, it is necessary to have a means of characterising surface composition with nm spatial resolution. This currently remains a significant challenge in nanoscale science and technology—there are few methods with genuine nanometre resolution that also provide information on surface composition. One of the most useful and straightforward approaches is to use friction force microscopy (FFM).[26] In FFM, lateral deflections of an AFM cantilever are measured. These are influenced by the strength of the frictional interaction between the tip and the sample. The friction force is, in turn, influenced strongly by the chemistry of the tip–sample interaction. A typical commercial AFM probe is fabricated from silicon nitride;

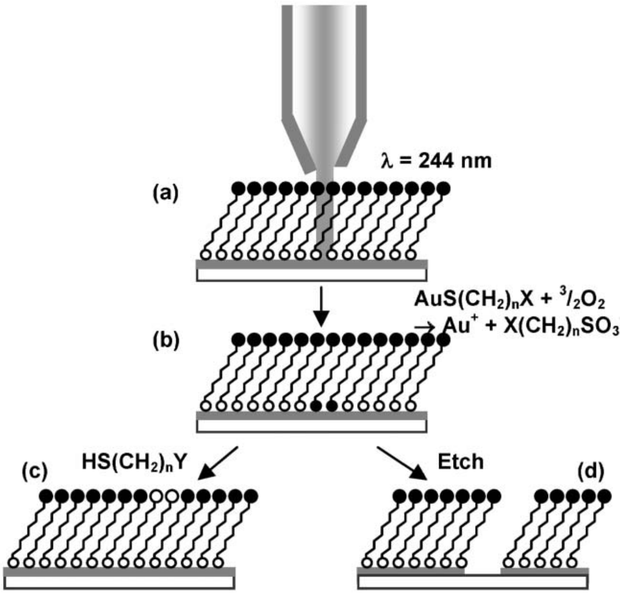


Fig. 6 Schematic diagram illustrating the basic principles of SNP.

the outer surface of the probe will thus consist of a thin layer of polar silicon dioxide. As the tip slides across a sample consisting of polar and non-polar materials, the tip will adhere more strongly to polar regions, leading to a larger friction force and a larger deflection of the cantilever. The strength of this interaction may be quantified in a variety of ways and used to measure the kinetics of surface modification processes, including SAM photopatterning, with nm spatial resolution.[27]

Near-field photopatterning of alkanethiol SAMs

A priori, therefore, one would expect to be able to exploit the full potential for spatial resolution offered by near-field lithographic techniques, with the resolution being determined, as a first approximation, by the diameter of the aperture in the NSOM probe. Fig. 6 illustrates the process schematically. An NSOM fibre, coupled to a suitable light source (a frequency-doubled argon ion laser, emitting at 244 nm is well suited to the purpose) is traced across the sample surface (a). Where the probe travels, the adsorbate molecules are exposed to UV light leading to their oxidation to alkylsulfonates (b). On immersion of the sample in a solution of a contrasting thiol, the oxidation products are displaced by solution-phase thiols, which adsorb at the surface forming a chemical pattern: the new adsorbate occupies the exposed areas, while the original adsorbate continues to occupy the rest of the surface (c).

Monolayers of carboxylic acid terminated thiols were formed and selectively exposed to UV light from a SNOM probe by Sun *et al.*[28] The samples were immersed, following exposure, into a solution of a methyl terminated thiol of similar length. The samples were imaged using AFM (Fig. 7). Conventional topographical images yielded no contrast because of the similarity in length of the adsorbate molecules; FFM images, however, yielded darker contrast (indicating lower friction) on the methyl-terminated lines than was observed for the carboxylic acid terminated regions between them (which being polar, interact more strongly with the polar material on the surface of the tip, increasing the strength of the frictional interaction). The line width in Fig. 7 is *ca.* 40 nm. This resolution is readily achievable on a routine basis. However, significantly better resolution is achievable. The smallest features fabricated to date by SNP have been 9 nm wide (nearly $\lambda/30$), and 20 nm structures are readily repeatable.[29] These are surprising outcomes, because *a priori*, one might have expected that the resolution limit would be defined by the dimensions of the aperture in the probe. To be able, routinely, to fabricate such small structures with probes that have, at best, an aperture diameter of 50 nm, is unexpected.

A possible explanation for this unexpectedly high resolution has been proposed. It has been observed that the resolution achievable in SNP is dependent upon the morphology of the underlying substrate. The substrates upon which our SAMs are prepared are typically polycrystalline, consisting of grains that have diameters in the range 10–100 nm. The grain size may be readily varied by altering the rate of deposition of the metal. As the grain size of the gold substrate decreases, so does the line width. This is illustrated graphically in Fig. 8(a). As the grains become larger, the line width increases, reaching a limiting value that is approximately equal to the diameter of the aperture in the probe. The limit of large grain size is represented by an atomically flat, epitaxially deposited gold film. For such a substrate, it was only possible to achieve a

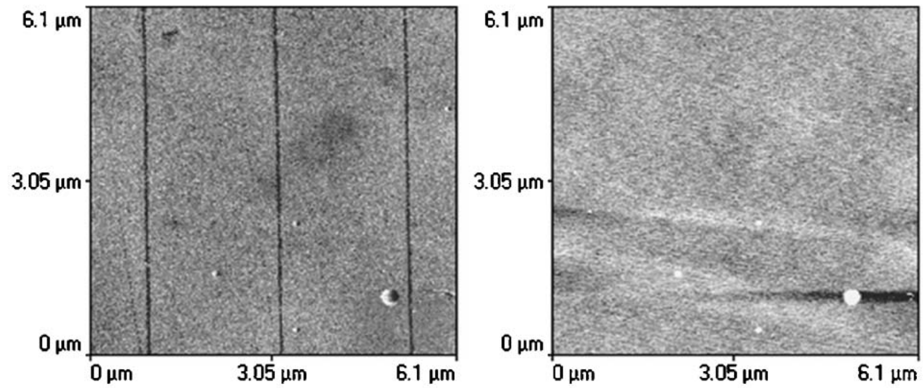


Fig. 7 FFM image (left) and AFM topographical image (right) showing lines of $HS(CH_2)_{11}CH_3$ written into a monolayer of $HS(CH_2)_{10}COOH$ using SNP.

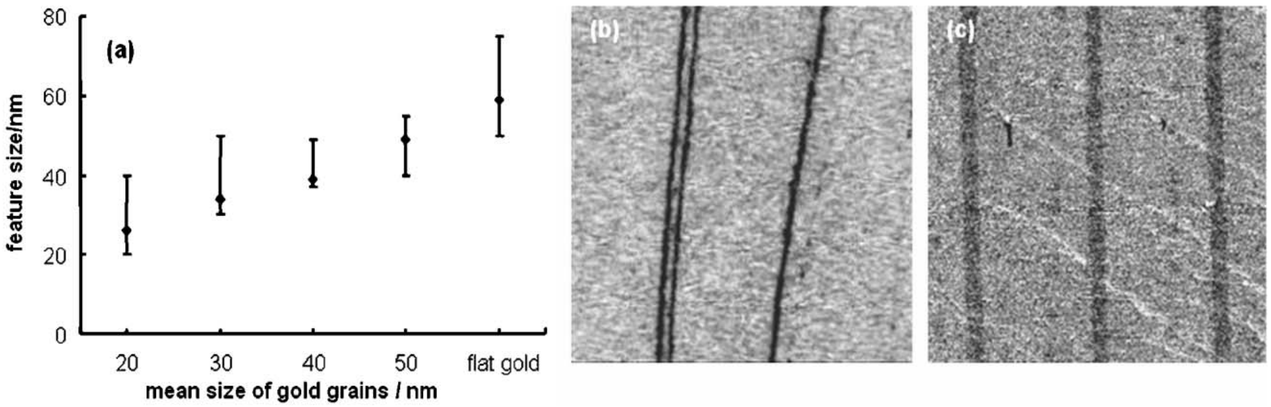


Fig. 8 (a) Variation in the line width as a function of the grain size of the gold substrate in SNP. (b) 20 nm lines written on a polycrystalline substrate (image size 1 × 1 μm^2). (b) 55 nm lines written on an epitaxially deposited substrate (image size 1.5 × 1.5 μm^2)

grain size comparable to the diameter of the aperture, *ca.* 55 nm (see Fig. 8(b)), whereas a line width of 20 nm is achievable on a substrate with a *ca*. 20 nm grain size (see Fig. 8(c)).

It has been suggested that the grains in the metal film effectively function like an array of asperities. As the SNOM probe traverses the sample, the electric field associated with the aperture interacts non-radiatively with the metal surface. There is an enhancement in the electric field strength as the probe travels over a grain—effectively an inversion of the "lightning-rod" effect described above. As the size of the gold grains decreases, one would expect the magnitude of the enhancement to become more pronounced, and this may well account for the increased resolution associated with the samples formed on gold films with small grain sizes. The observation of a resolution close to the aperture diameter for the epitaxially deposited gold film, in contrast, is also consistent with this hypothesis. It is significant to note that the best resolution was obtained for a polycrystalline film capable of being deposited rapidly and straightforwardly on a variety of types of deposition equipment, while for DPN, for example, the best resolution is obtained on atomically flat substrates, which require more strenuous control of the deposition conditions.

While this may seem at first sight to be a phenomenon that is rather limiting, in fact "lightning rod" effects are observed with a range of materials and they are not restricted to gold. Moreover, they may be capable of exploitation for near-field imaging—by forming samples on polycrystalline substrates, that effectively constitute arrays of nanoantennae, it may be possible to obtain improvements in near-field image resolution.

Illustrations of nanofabrication by SNP

SAMs patterned by SNP are useful as resists for the nanometre scale etching of metals. This is illustrated schematically in Fig. 6(d). The process is very similar to that used to form molecular patterns, but in the final step, instead of being immersed in a solution of a contrasting thiol, the sample is placed in a solution of an etchant for the underlying substrate. The etchant displaces the oxidation products from the surface and erodes the underlying metal. This kind of application for patterned SAMs was pioneered by George Whitesides in connection with micron-scale patterns generated by microcontact printing,[30] but it is very effective when transferred to the nanometre scale. The Whitesides group developed a ferri/ferrocyanide etch agent for use with gold in conjunction with micropatterned thiol resists, and when this was applied to nanopatterned SAMs fabricated by SNP, it was possible to fabricate 50 nm trenches.[31] Recently, however, an even milder etch has been developed, which is based on a solution of mercaptoethylamine in ethanol, with a drop of ammonia added.[32] Using this surprisingly innocuous organic reagent, it was possible to etch trenches that were only a few tens of nm wide into gold films. It seems likely that the mercaptoethylamine coordinates to gold as a bidentate ligand, solubilising surface atoms where the metal is not protected by a layer of thiol adsorbates. Fig. 9 shows the result. Three lines have been written into a SAM of mercaptopropanoic acid, which has been subsequently immersed in a solution of mercaptoethylamine, leading to etching of the gold underlying the oxidized regions. The lines have sharply defined edges. Fig. 9 also shows an AFM image of a single line etched in this way at higher magnification. Analysis of a line section taken through the trench indicates that the full width at half maximum depth (FWHM) is 30 nm, although subsequent analyses by electron microscopy suggest that the dimensions determined by AFM may be over-estimated by *ca*. 20% because of the convolution of the tip with the surface profile. The etched features clearly have sharp edges. This approach is attractive because it delivers very high definition using mild (non-hazardous) and inexpensive reagents, and because the number of processing steps involved is low.

A slightly different approach to the fabrication of three-dimensional gold structures was recently demonstrated in studies of thiol-stabilised gold nanoparticles.[33] The thiol molecules, that stabilise the nanoparticles and prevent coagulation, may be oxidised on exposure to UV light. It was found that the consequence of this was a destabilisation of the nanoparticles, leading to their coagulation. Selective exposure of the nanoparticles could be achieved by irradiation through a mask, or by exposure to UV light from a SNOM probe. The best results were achieved when a bilayer of nanoparticles, formed by Langmuir–Schaeffer deposition, was used as the resist. The

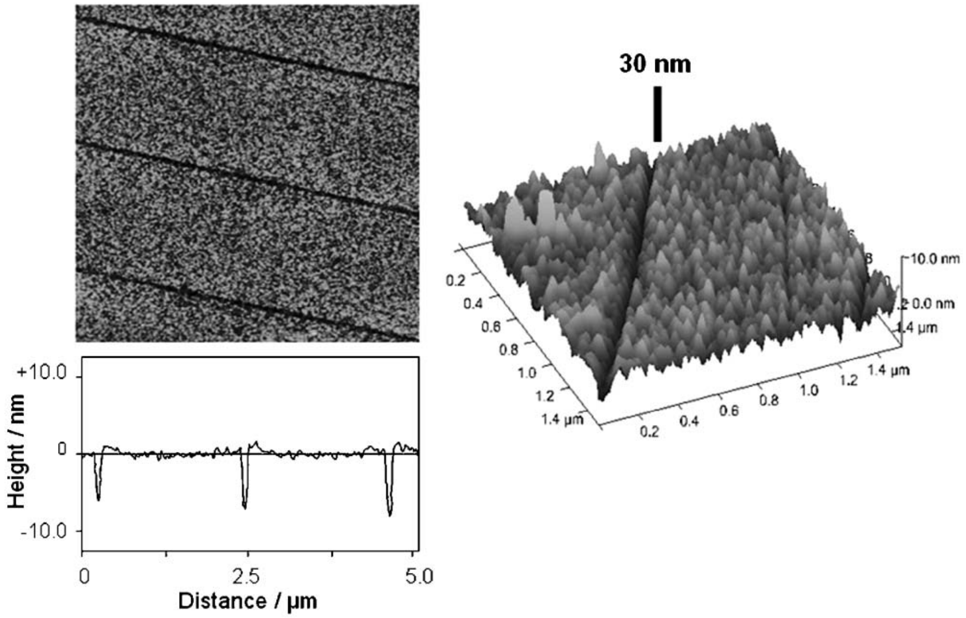


Fig. 9 Left: AFM image and line section through nanotrenches etched into gold. Right: horizontal projection of a single trench.

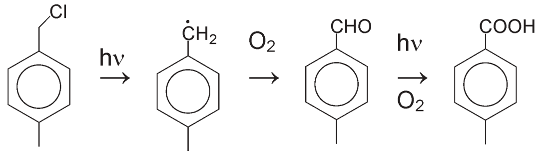
unexposed nanoparticles could simply be removed by rinsing of the sample, leaving behind well-defined nanolines, only 60 nm wide and 7 nm high. Although the electrical properties of these lines have not been characterised, they have significant potential in a number of applications. The attraction of the fabrication method is the simplicity of the fabrication process, which only involves two steps.

Polymer nanoparticles have been patterned very simply by patterning the adhesiveness of a SAM and functionalising the nanoparticle. For example, carboxylic acid terminated thiols were selectively photo-oxidised and replaced by amine-terminated adsorbates, to which aldehyde functionalised polymer nanoparticles could be attached.[34]

Applications of SNP to other substrates

All of the illustrations of SNP described thus far are of monolayers formed on gold substrates. If the method only worked in these circumstances it would be very limited. However, the basic principle underpinning the high resolution achieved for the thiol-on-gold system was the excitation of a specific photochemical reaction in a group distributed with monolayer coverage on a solid surface. In fact, there is a very wide range of systems that fits this description. Hydrogen passivated silicon surfaces are one system that fits it well. Etching of silicon surfaces in ammonium fluoride yields surfaces that terminate in Si–H bonds. These are reactive towards alkenes under irradiation by UV light. The functionalisation of hydrogen-passivated Si by decene has been demonstrated in an experiment in which the SNOM probe was immersed in a thin film of fluid reagent. The resulting structures were etched using potassium hydroxide. The alkylated regions resisted the etchant, while the interveneing regions were etched, yielding three dimensional nanostructures.[34]

An alternative, but more sophisticated approach is to utilise a monolayer of adsorbates that terminates in a photo-active group. Monolayers of chloromethylphenyltrichlorosilane (CMPS) adsorbed onto the native oxide of silicon are one such system. In bulk studies, benzyl chloride has been shown to undergo a photolysis at 250 nm to yield a benzyl radical which is converted, in the presence of oxygen, to benzaldehyde and then, on continued exposure, to benzylic acid. In principle, it was hypothesised, it might be possible to initiate similar photoconversions in CMPS monolayers:



Monolayers of CMPS were formed on the native oxide of silicon and exposed to light from a frequency-doubled argon ion laser (244 nm) and characterised by XPS, which confirmed that chlorine was eliminated and oxygen incorporated to yield first an aldehyde and then a carboxylic acid.[35] At very high exposures desorption of the adsorbate was found to occur. Nanopatterning was then attempted using a SNOM coupled to the same UV laser to initiate photochemistry. Lines only 45 nm wide were formed rapidly, and imaged using FFM. The objective of the work was to form carboxylic acid functionalities and the efficacy of the process for this was tested in a variety of ways, by activating the surface using a carbodiimide reagent in combination with *N*-hydroxysuccinimide, to form an active ester and render it reactive towards amine groups. Proteins, amine-functionalised nanoparticles and DNA molecules were all immobilised. Fig. 10 shows lines of carboxylic acid groups prior to derivatisation, together with an array of 70 nm DNA spots formed at 500 nm centres by near-field exposure followed by carbodiimide activation and derivatisation with DNA. DNA arrays are widely used in biological analysis. However, the density of features in the array in Fig. 10

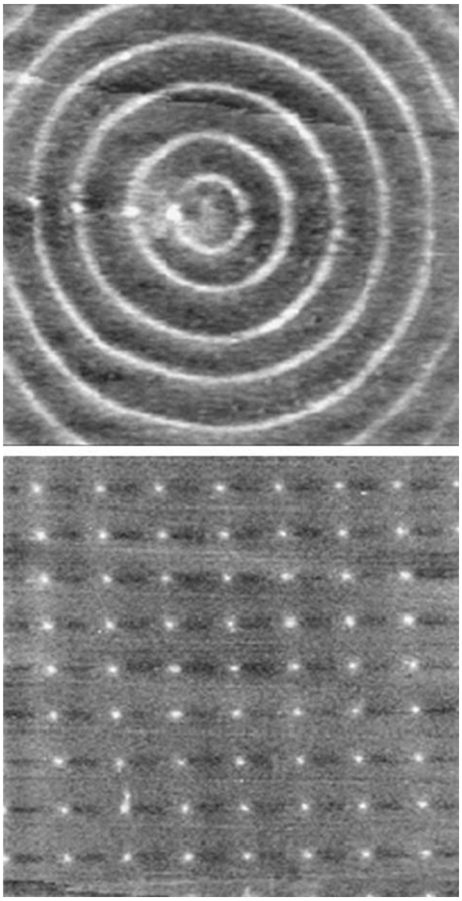


Fig. 10 Top: FFM image showing patterns of carboxylic acid groups formed in a CMPS monolayer by SNP. Bottom: array formed by covalent coupling of DNA to SNP-fabricated carboxlyic acid spots. Both images are $4 \times 4\ \mu\mathrm{m}^2$.

is such that 40 000 spots could be fabricated in the area occupied by a single spot in a conventional array, while the spacing is nevertheless such that they could be detected optically using conventional far-field methods.

At high exposures, near-field lithography caused desorption of adsorbates leading to the formation of oxide nanostructures, reflecting the behaviour observed in the far-field.

The attraction of processes such as this is their chemical selectivity. Simply by varying the exposure, it is possible to select either an aldehyde product or a carboxylic acid product, or to desorb the adsorbate. This flexibility is illustrative of the enormous potential offered by near-field methods for nanometre scale surface functionalisation: it is a degree of specificity that is inaccessible by any other lithographic method and which presents the attractive possibility of being able to execute specific chemical transformations (*i.e.* synthetic chemical steps) in a spatially defined fashion, with a resolution approaching the dimensions of individual macromolecules.

Future prospects

While the use of near-field methods to carry out lithographic manipulation of surface structure is very much in its infancy, the potential offered is considerable. Because of the general perception that near-field methods are "difficult", and the smaller numbers of SNOM instruments available, researchers may be deterred from exploring them. However, it is important to remember that in lithography, there is no longer a requirement to collect an optical signal—the SNOM simply provides a very small light source—and this makes the lithographic experiment substantially more straightforward than near-field microscopy. Because of the broad range of synthetic chemical methods that is available based upon photochemistry, and because of the evidence that now exists for the high resolution of near-field methods, approaches based around SNP are very well placed—perhaps uniquely so if exploited to their full potential—to facilitate the unification of top-down and bottom-up fabrication.

There are a number of developments that may be significant in the context of the future exploitation of near-field methods. First, there is growing interest in apertureless methods for near-field microscopy and this is now beginning to bear fruit. Given the enormous resolution improvements that are capable in apertureless excitation, because of the substantially enhanced electric field confinement, and also the potential for signal enhancement, because the large losses associated with transmission through a sub-diffraction limit aperture are eliminated, it seems likely that apertureless techniques may facilitate significant further advances in the capability of near-field lithography. While field enhancements may be large beneath the tip, it will be a major problem to restrict surface modification due to far-field exposure. The magnitude of the balance between increased exposure beneath the tip due to field enhancement, and slow but continuous degradation over a macroscopic area, needs to be weighed carefully. Initial findings from Royer's group are very promising. They have demonstrated that lines only 50 nm wide may be written into a photo-sensitive polymer.[36] Their sharp, narrow structures compare very favourably with the diffuse structures fabricated in similar materials by other workers using apertured approaches. However, the problem of far-field exposure is undeniably a critical one. The solution perhaps lies in the utilisation of processes such as two-photon absorption, which has recently begun to attract a great deal of interest in more conventional lithographic applications. Two-photon processes have cross-sections that scale with the square of the intensity of the illumination, yielding a substantial enhancement in spatial resolution. Combined with a field enhancement of two to three orders of magnitude resulting from the use of an optical nanoantenna, the result may be a very substantial localisation of excitation that effectively negates the influence of far-field exposure.

A further consideration is that most of the work to date has focused on systems that are not really optimised for photochemical synthesis. For example, the selection of a thiol system for the initial SNP studies certainly provided a resist that was confined very narrowly perpendicular to the surface, but nevertheless relied upon a photochemical reaction that, it is clear with hindsight, is not very fast and, moreover, is tied to a rather narrow class of adsorbates. The CMPS system is much more attractive in that the chemical reaction is still confined to a single functional group distributed with monolayer coverage, but is not confined to a particular substrate (monolayers that terminate in a similar terminal group may be prepared on a variety of substrates). Moreover, there are many photo-active groups that could be used in a similar way that are more reactive, and there is significant scope for tailoring the properties of the adsorbate to engineer absorption at a specific wavelength, and to enhance the cross-section for absorption at that wavelength.

In many ways, therefore, work to date has only scratched the surface of what is possible, in terms of both the range of chemistry that is accessible and the resolution that may be achieved through, for example, a combination of apertureless and two-photon approaches. The future for near-field lithography thus appears to be a bright one.

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