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A Split-Tip Proximal Probe for Nanoscale Deposition of Molecules with Controlled In-Plane Orientation

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Abstract

Nanoscale materials are now fabricated by a variety of means, but the dominant methods rely on self-assembly or advanced lithography. These and other fabrication schemes, especially self-assembly, can create structures in which the molecular orientation perpendicular to the surface is controlled by the chemistry. This is important for functionality. We present the first step – a split-tip nanoprobe – of a method to take this control of orientation one step further – so that the molecules can also be locally oriented in the plane of the surface. The method allows variation of the orientation on a <100 nm length scale, so that nanoscale functionality that is based on the relative orientation of molecules can be obtained. This is needed since a uniform layer is not a device. This is a powerful concept for high performance molecular devices, since the properties of molecules are highly anisotropic. It also allows the fabrication of many independent structures close together on a surface, as has been the successful paradigm in microelectronics. The 'nanopoling' scheme that we propose should be much more effective at orienting molecules than current poling methods due to the larger electric field that can be generated locally. This advantage is in addition to the obvious resolution improvement.

Introduction

Many complex materials and polymer or other molecular-based electronic devices depend upon the orientation of the components for their properties. The interface properties are crucial to performance, and are determined by the orientation of any non-symmetric molecule involved. Orientation also matters within the film. For example, problems of orientation in conducting polymers leads to poor electrical performance, [1-3] and nonlinear polymers must usually be poled to yield some degree of orientation so that they function well. [1] We describe a technique utilizing nano-poling during deposition to orient the molecules in-plane. It will improve performance in these systems due to the ability to orient to a much higher degree, since the orienting fields can be higher and the molecules are oriented while they are more mobile. The very high degree of orientation will allow new devices based solely on the orientation of one asymmetric species of molecules. We present here the fabrication and electric field modeling of the central tool to enable this technique – the split-tip probe.

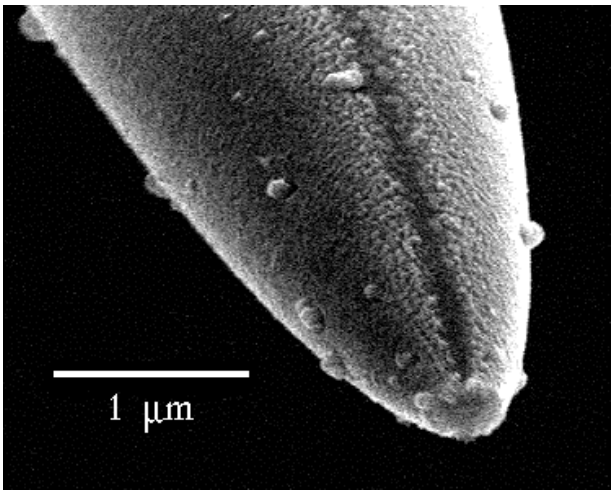

Figure 1. The split-tip probe. The electrodes are on the left and right sides, and the aperture is visible at the bottom.

Especially in devices, but also in certain nano-structured films, lateral resolution in the plane of the film is also required. Resolution can be obtained with lithography, using lift-off or etching, but it can also be accomplished during growth with the help of a scanning proximal probe. A 'smart-mask' technology based on the insights and parameters from the scanning-probe should yield a method rapid enough for commercial fabrication. In this paper we concentrate on the scanning probe approach to attach molecules to a surface with fixed orientation, and in particular the design of the probe for this purpose. The probe not only guides the deposition, but can characterize the quality of the resulting material by (1) measurement of topography by the NSOM-like scanning probe, or (2) measuring orientation with polarization-dependent NSOM imaging with the probe that is also used for deposition.

The key aspect of the oriented molecular deposition system is a split-tip probe, which is mounted onto a standard scanning proximal probe microscope. In particular, the split-tip probe consists of two electrically isolated and independently contacted metal electrodes deposited on opposite sides of a tapered optical fiber, similar to those used for near-field scanning optical microscopy (NSOM). An electron microscope image of one of these split-tip probes is shown in Fig. 1. We use Al or Au for these tips. The probe is mounted onto an existing NSOM system. The NSOM system has the required optical hardware for coupling laser light into the region between the split-tip electrodes, which is exactly where it is needed for initiating the bonding to the surface.

We begin with a comparison to existing technologies and potential applications of the split-tip probe based technology, then detail a deposition scheme that can make use of the split-tip probes. The method of probe fabrication is presented next, followed by calculations of the electric field near such a probe, which show that orientation of molecules is possible, and finally a note on how the probe can be used for characterization in addition to deposition.

Comparison to Existing Technologies

The following comparison will concentrate primarily on scanning probe efforts for nanoscale fabrication. Proximal probe lithography has been used for several years. Early work included using an scanning tunneling microscope (STM) as an electron source with e-beam resists [4] or for electron-assisted chemical vapor deposition, [5] single atom manipulation at low temperature [6] or room temperature [7, 8], the creation of gold bumps on a surface with an STM current pulse, [9] and the growth of single layer high gold terraces on the bottom surface of a gold film with hot electrons injected from an STM tip, and their observation with ballistic electron emission microscopy (BEEM). [10-13] More recent examples of high lateral resolution patterning with proximal probes includes optical modification of materials with a near-field scanning optical microscope (NSOM), [14, 15] and 'dip-pen' nanolithography with an atomic force microscope (AFM). [16] Although the resolution of many of these probe methods is very high, the interactions with the samples are symmetric, so lateral (in the plane of the sample) orientation cannot be controlled. The proposed project addresses this issue by using a nonsymmetric 'split-probe' to control orientation through a proximal probe

interaction while maintaining nanometer-scale resolution. This added dimension of control represents a significant advance.

A problem with proximal probes for large-scale patterning is that they are usually slow. Several approaches were proposed including rapid motion of the substrate -- a spinning disk, [17, 18] utilizing many probe microscopes in parallel, [19, 20] and using the microscope only for small, specific regions on the sample as has been done for metrological purposes on an IBM process line. [21] Although these ideas can be made to work, one must still be very concerned about the complexity of the systems and the long-term reliability. Tip wear will always be a problem with scanning probe systems. We therefore believe that the proximal probe should be used where it gives the most advantage – in the developmental and model-building stages. Later, industrial-scale manufacturing stages should be performed with more naturally parallel and robust systems. Our method of oriented deposition should be extendable to a 'smart-mask' system.

Potential Applications

The split-tip probe enables the fabrication of highly oriented, nano-scale-patterned materials. The greatest impact will probably be for electronic materials, where the orientation will increase the conductivity and may help to reduce the voltages required for operation of polymeric electronics. There should also be an impact on other materials where an anisotropic optical response is desired, or in biomedical applications. The latter application requires molecular orientation for cellular recognition. These are discussed in more detail below, and serve to define the materials systems that we will investigate.

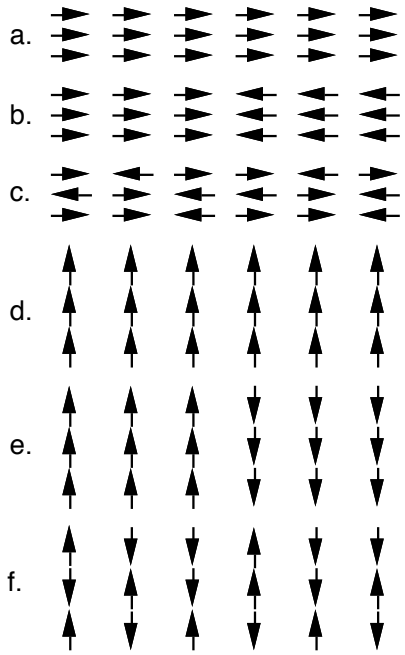

Figure 2. The arrows indicate which way the molecules are oriented in several configurations, which will be studied, as described more fully in the text. The current flows from left to right. These are schematic: there will be many more molecules in each direction than shown.

High Performance Conducting Polymer Films. The conductivity of conducting polymer films is improved by a process called poling, in which a large electric field is applied to the material to partially align the molecules and dramatically increase the conductivity. The higher local fields provided by our probe and poling during growth should result in almost all of the molecules oriented in the same direction while they are defined into wires on the nanometer scale. These are two major impacts in the conducting polymeric materials arena. Figure 2 shows example structures that could be fabricated. The material is deposited in the gap between the contacts. The size of the structure that can be made without manual coarse adjustment is limited by the instrument scan range of ~25 microns.

Conducting polymers are typically semiconductors with similar bandgaps due to the common π-conjugated bonding found in these polymers. [1] The materials display a broad range of conductivities. The conductivity is strongly dependent on the morphology, [22, 23] which consists of ordered domains separated by disordered regions [1-3] in material prepared by standard practices. Our deposition method should yield wires with nearly perfect orientation, due to the strong poling field we can use during growth. These should show much higher conductivity, which we will measure, and the ability to carry large current densities with a long lifetime.

New Device Opportunities The ability to orient a conducting polymer molecules virtually 100% in the same direction, which can vary on a nanometer-scale length, allows new possible device configurations that depend

upon the orientation of an asymmetric molecule rather than different doping of regions of less-ordered molecules. The field provided by the probe should be sufficient to prevent the depolarization field from previously deposited molecules from affecting the orientation of later molecules. Some example structures are shown in Figure 2, where the arrows represent the direction of the permanent dipole moment of the molecules (much enlarged). We can investigate conduction along the molecules, expected to be good, with all molecules aligned, Figure 2(a), with an interface, that should act as a potential barrier from an analysis of the electrostatics, Figure 2(b), and with both orientations in a film produced by alternating the field direction during the deposition process, Figure 2(c). Studies of the properties when molecules are oriented perpendicular to the current flow direction will also be possible, with a similar array of orientation possibilities, Figure 2(d-f).

Reduced Driving Voltage. Most conducting polymeric devices such as polymer LED's require a very large driving voltage. This reduces efficiency and inconvenient power supplies. Our technique can impact this area by providing a means to reduce drive voltage, improve the quantum efficiency by reducing defect quenching [24] and increase the capability for high current densities so that electrically pumped polymer laser diodes can be fabricated. [25] The addition of secondary molecules near an electrode [26] to improve efficiency and lifetime [27] is also possible. This could be done by combining the 'dip-pen' lithography with our orienting capabilities. Optimization of the electrode/polymer interface, especially the band offsets, [27, 28] will reduce the drive voltage. The NSOM technique (with the deposition probe) can be used to create light emission maps of the device, to test that the structures are behaving as expected.

Electrical Connection to Tissue. When cells are adjacent in a tissue, they recognize each other by the proteins displayed. A cell constructs a protein tunnel that connects its ion channels to those of its neighbor so that when it signals (changes the ion current pattern), the next cell receives the message. There are many types of ion channels in cells, but only like-types are connected. Thus, one way to optimize specificity in communications between man-made electronics and tissue is to mimic the protein distribution of a particular ion channel of interest, using the orienting capabilities of split-tip probe fabrication, and let the cell build the connectors.

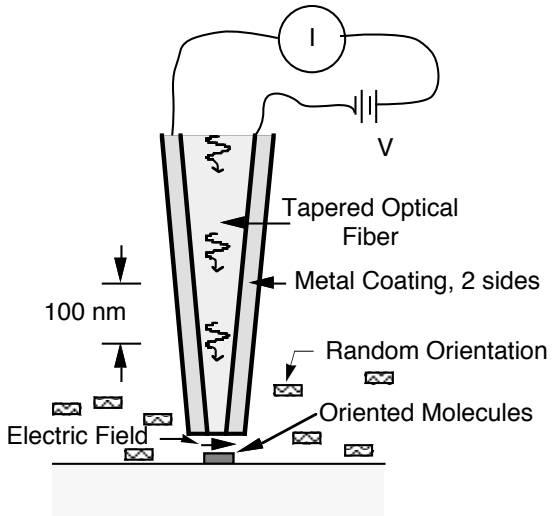

Figure 3. A schematic of the probe illustrates the major features.

The Deposition Scheme

A schematic of the probe tip near the sample is shown in Fig. 3. In this cut-away view, the electrodes are on the left and right sides of the tip. The electric field is localized in the region of the split, and is highest where the split is narrow – near the tip apex. Molecules that are in solution will be oriented where the field is high, but not elsewhere. When the tip moves to a new location, it aligns the molecules, then initiates the linking to the sample with a light pulse (or current pulse). The tip then moves to a new location, orients the molecules as they should be in the new location, and links them to the surface. It is important that molecules not under the probe tip do not attach to the surface, since they are not oriented. The schemes for insuring this are below. The molecules are shown in solution. This is not necessary. They could also be deposited 'dry' onto the surface, those in the regions of

interest be rotated by the field and linked to the surface, then the remainder washed off. Another alternative is to load the tip with molecules as in the 'dip-pen' lithography scheme, [16] oriented and attached as in liquid, then another molecule chosen for a different position.

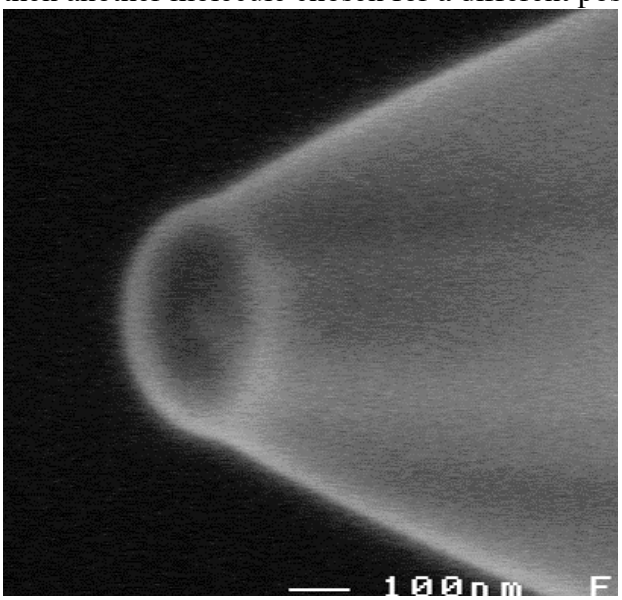

Figure 4. SEM image of a larger-aperture tapered fiber fabricated by the heat-and-pull method. Note the flat cleaved end that is formed when this fabrication scheme is used, as

Probe Fabrication

Our 'split-tip' probe resembles an NSOM probe, and it is fabricated using the same process as our NSOM tips. We use either a Sutter Instruments puller, modified to work better with fibers, [29-32] or chemical etching [33] to taper the end of an optical fiber. We need to pull the fibers when we want a large separation of the electrodes, since the fiber gets a flat face as it cleaves in the fiber pulling apparatus, as can be seen in Fig. 4. This shape contrasts with the sharp point at the tip of properly-etched fibers. Thus, if the electrodes are to be brought in close proximity to the surface, they need to be close together with etched fibers, but may be further apart when pulled fibers are used. Etched fibers are more reproducible to fabricate in large quantities, and have a higher optical throughput. We initially used only pulled fiber probes for the fabrication of split-tip probes, since we were concerned that the electrodes might short near the tip, but we now use both types without shorting problems.

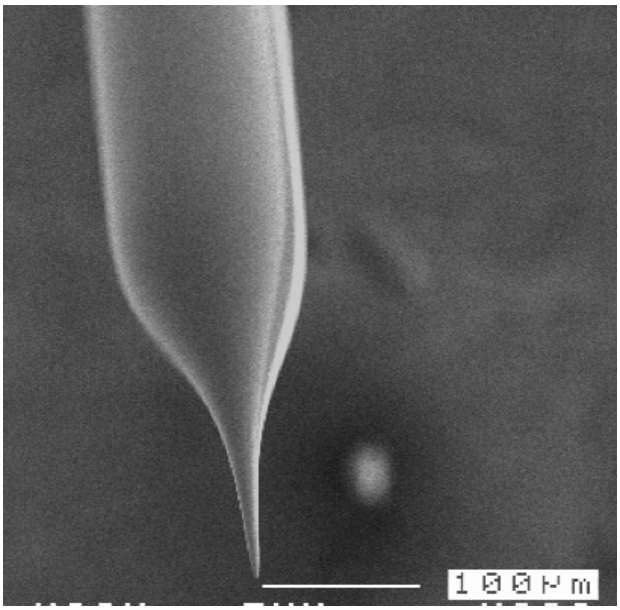

Figure 5. A split-tip probe, showing the entire tapered region.

Once the fibers are shaped, metal is coated on one side, then the fiber rotated 180°, and the other electrode is deposited. This forms a split metal structure with the two metal sides electrically isolated. The metal coating must be thin so that the two sides do not short together. Our probe-holding fixture in the deposition chamber allows an accurate flipping of the probes in vacuum, and three different source materials can be used during one pump-down. We use Al or Au. Following the initial deposition, a thicker coating of gold is applied to the contact regions on the shank of the tip. A close-up view of the split-tip probe can be seen in Fig. 1, and a view at lower magnification is given in Fig. 5.

Various tests are needed to insure that the electrodes are not shorted and that the probe is in proper working order. A voltage is applied to one side of the split tip while the other side of the probe is brought to a virtual ground through a high gain current preamplifier. We have two leads on each side of the tip shank to insure that contacts are made. The tip is mounted in an NSOM system with a known orientation of the probe split, and the sample approached. Lateral force feedback is used to regulate probe-sample distance. This is the same as that used in NSOM, with a sub-nanometer lateral tip oscillation, sub-nanometer to 10's of nanometer probe-sample distance during regulation, and ~10 nm lateral resolution (typically better than 1 nm

vertical resolution). Once the microscope has settled (thermal drift and piezoelectric creep) and particular region for deposition has been located, we can begin.

Electric Field Near the Tip.

The flat end of the probe defines the deposition region between the electrodes. It size can be from several hundred nanometers down to ~10 nm. We can estimate the field strength if we assume a flat capacitor model. For example, a 50 nm tip with 0.5V applied would have a field of order 10^7 V/m. This is a very large electric field, and it is therefore not surprising that we have, on occasion, found that the probe tip is damaged by the high fields. We observe this as an irreversible change in our ability to control the polarization of the light emanating from the probe. It results from damage to the silica. The result illustrates two points: (1) If large voltages are required, a larger electrode spacing is required. We are in the process of quantifying the maximum allowable voltages. (2) We can apply very large fields to the molecules that are being oriented. This is a common occurrence in nanoscale science, when distances get small, and results in new physics as energetic electrons can be injected into materials – potentially causing damage. [11-13, 34, 35] These fields can allow access to nonlinearities in the electric field interaction. We will probably not need to use fields this large for orienting molecules, but it is important not to exceed the probe damage thresholds in order not to cause artifacts in the following optical characterization. The high fields may be useful for inducing bonding to the surface, although we do not expect to require them.

Optical Characterization.

The split-tip probe permits optical characterization of the deposited material. As has been mentioned, the probe must be asymmetric for use in lateral orientation. Our 'split-tip' probe resembles an NSOM probe, except that the metal coating on the outside is split into two parts that are electrically isolated. As such, it can be used as an NSOM tip for optical imaging as a characterization technique. The NSOM topography will also be used as the indicator of material deposition: both where it should and should not be. Polarized light will be used to detect sample anisotropy and hence the quality of orientation. We have been able to control the state of polarization of light emanating from a *split-tip probe* from linearly polarized (>100:1) in any direction, or circularly polarized. The large anisotropy expected in the deposited materials will permit the use of a simple anisotropy analysis system comprised of polarized illumination through the probe with an analyzer in the far-field collection system. For a conducting polymer film, this optical anisotropy data related to orientation should corroborate the electrical properties, and provide insights for the further improvement of the material. Specific questions include the spatial and size distribution of the ordered regions and a quantification of the charge carrier scattering at the interface of mis-aligned molecules. The spatial distribution of light emission would also be mapped for the light emitting polymers by simply collecting the light through the NSOM probe. The results of the optical characterization are available in a matter of minutes after deposition, making the evaluation procedure very simple. This, and the flexibility of distance adjustment, is why it is easier to develop the technique with a probe microscope.

Summary.

We have described a novel split-tip probe, which can be used to explore the possibility of depositing molecules with specific in-plane orientation that can be controllably varies over 10's of nanometers. It is expected that the development of this method will open new venues for the fabrication of complex materials and, in particular, novel polymer electronic materials and devices or biological interfaces.

Acknowledgements.

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