

and five parts per billion for many VOCs, and responded rapidly and reversibly to a range of concentrations in the presence of water vapour.

Although this sensor system holds great promise for the future, the current study describes an early phase of breath-test development. Despite efforts in this and other reports to identify a unique lung cancer biomarker profile in breath, a consistent model has not been found. Thus, the concentrations and types of discriminatory volatiles that a lung cancer sensor would need to detect are not fully known. Furthermore, because the current study enrolled mainly advanced-stage lung cancer subjects and healthy controls, it remains unclear if the system could also

distinguish the breath of people with early-stage lung cancer from those with other lung diseases. Moreover, to know whether it is simple and easy to use, the system needs to be tested outside the hands of its expert creators. Future work should focus on clarifying the nature and origin of the breath VOC biomarkers for lung cancer, refining the sensor technologies based on the discovered biomarkers, and applying these improved technologies to a broader group of subjects.

There is a great deal of excitement and anticipation in the breath analysis community. Advances in the technologies available to researchers, and the growth in the number of interested labs, are certain to lead to breakthroughs that can be translated

into clinically useful medical tests for a variety of diseases. The present work on gold nanoparticle sensors is welcomed in this direction. □

Peter Mazzone is in the Respiratory Institute at the Cleveland Clinic, 9500 Euclid Avenue, A90, Cleveland, Ohio 44195, USA.
e-mail: mazzonp@ccf.org.

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NANOPATTERNING

Surfaces feel the heat

Thermochemical lithography is able to produce features just 28 nanometres wide on polymer surfaces.

Amar S. Basu and Yogesh B. Gianchandani

The ability to pattern materials at submicron and subnanometre length scales is crucial in many areas of nanotechnology. The wide landscape of top-down patterning methods that have been developed to meet this challenge can be categorized into three groups: photolithography, direct-write methods, and methods based on a scanning probe. In traditional photolithography, which uses optical masks to transfer light patterns to a photoresist, the smallest feature size is limited by diffraction to be about half to a quarter of the wavelength of the light used. The demand for smaller feature sizes has prompted the use of shorter wavelength sources such as deep ultraviolet (around 200 nm), extreme ultraviolet (10–13 nm), and X-rays (around 1 nm)¹. Semiconductor companies are also turning to liquid immersion, optical interference and other techniques to extend resolution into the 20–50 nm range².

Direct-write methods such as electron-beam and ion-beam lithography use focused beams of particles with small de Broglie wavelengths to achieve high resolution¹. These methods avoid the use of masks, but offer lower throughput. Probe-based nanopatterning methods, in contrast, rely on the local interactions between a sharp tip and the sample to alter the surface by mechanical, chemical, thermal or fluidic means as the tip is

scanned over the surface. Methods developed so far include the use of atomic adsorption³, tunnelling fields and currents³, near-field light⁴, mechanical forces⁵ and dip-pen lithography⁶.

Thermochemical lithography is a relatively new probe-based approach that involves heating the tip on a scanning probe (Fig. 1) so that it catalyses a chemical reaction on the substrate. On page 664 of this issue, Franco Cacialli and co-workers⁷ at the London Centre for Nanotechnology, University College London, Lancaster University and the University of Pisa report that thermochemical lithography can be used to pattern an electroluminescent polymer with nanoscale resolution.

This work highlights two of the most promising aspects of thermochemical lithography: the potential for high resolution and the ability to pattern a wide range of materials. In probe-based approaches to patterning, the resolution is determined by the spatial extent of the tip-sample interaction rather than the diffraction of light. Depending on the type of patterning involved, the factors that influence the resolution include the tip geometry, tip-sample spacing, and the dependence of the relevant interaction on this spacing, diffusion, substrate properties and biasing. Often, the best resolution that can be obtained is similar to the tip diameter.

Surprisingly, Cacialli and co-workers are able to achieve feature sizes of 28 nm, which is almost two orders of magnitude smaller than the diameter (5 µm) of the Wollaston wire they used for patterning. This can be attributed to two factors: the contact area between a hemispherical tip and a flat surface is much smaller than the radius of the tip; and a phenomenon known as spatial thresholding (which ensures that only a small region of the surface is hot enough for the thermochemical reaction to proceed⁸). Other examples of sub-tip resolution with thermochemical lithography included line widths of 12 nm on very thin films⁹.

A second promising feature of the thermochemical approach is the wide range of materials that can be processed. The application of heat is a universal method for the chemical modification of polymers, changing the solubility and surface properties through thermally-activated cross-linking, deprotection, substitution and other mechanisms. In addition to the large number of thermally sensitive polymers that are already available, temperature sensitivity can be conferred on other materials by adding commercially available cross-linker additives. Furthermore, if the temperature of the probe can be controlled, it may be possible to simultaneously process multiple materials, each addressed by a distinct

processing temperature. Cacialli and co-workers patterned poly(*p*-phenylene vinylene) (PPV), an electroluminescent polymer that is increasingly being used in polymer light emitting diodes and photovoltaic cells.

Although the future of thermochemical lithography seems promising, a number of challenges still have to be addressed. Like other scanning probe techniques, thermal patterning can modify a surface, but not necessarily the entire thickness of the film. The sub-surface heat conduction is largely isotropic, and for thicker films this may result in larger features with overhanging profiles that are undercut during removal of the untreated polymer or subsequent processing steps. The mechanical collapse of nanoscale resist features with high aspect ratios, often due to capillary forces associated with wet processing, has also been a challenge. Line edge roughness¹⁰ — due to spatial and temporal temperature fluctuations, resist chemistry and other chemical processes — could also limit the ultimate resolution of thermochemical lithography.

Throughput will be another significant challenge, and although thermochemical lithography is unlikely to compete with optical methods in this regard, write speeds have increased from less than a micron per second to more than a millimetre per second⁹. It remains to be seen if the ultimate limit on the write speed will depend on the reaction rates of the material being patterned or on the thermal transport properties of the overall system.

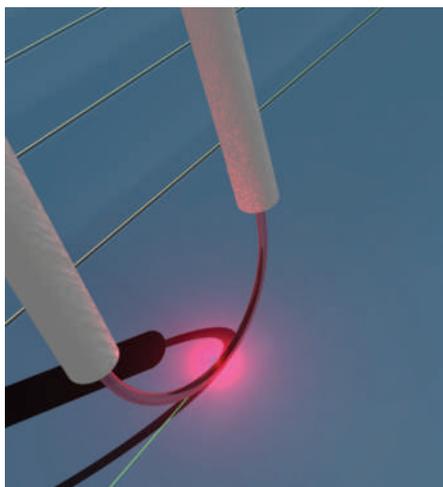


Figure 1 | Artist's impression of thermochemical lithography. Cacialli and co-workers were able to produce features with line widths as small as 28 nm by scanning a heated wire over a polymer surface⁷. The wire, which is made of platinum and rhodium, has a diameter of 5 μm and is heated by passing a current through it.

A robust system for thermochemical patterning will also require tight tolerances on a number of parameters. For example, the contact force between the tip and the sample influences not only the thermal heat transfer but also the mechanical or thermomechanical deformation of the film. Atomic force microscopy systems can maintain precise force feedback control, but only if the tip geometry, spring constant and angle of attack of the probe

are maintained throughout the duration of the scan. The probe temperature will also need to be precisely calibrated and controlled, as reaction rates are often exponentially related to temperature. Other practical aspects to explore include Joule expansion of the material and the effect of wetting films that form between the tip and the sample.

The field of thermochemical lithography is young and holds much promise for patterning unique materials at the nanoscale. Although factors such as the limit on throughput might restrict its usage, its simplicity and applicability to a wide range of materials means that it will find its niche in the nanopatterning tool set. □

Amar S. Basu is in the Department of Electrical and Computer Engineering, Wayne State University, Detroit, Michigan 48202, USA. Yogesh B. Gianchandani is in the Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, Michigan 48109, USA. e-mail: abasu@eng.wayne.edu; yogesh@umich.edu

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SPINTRONICS

Shedding light on nanomagnets

The magnetism of semiconductor nanocrystals can be controlled by shining light on them, which could have applications in information storage and processing.

Igor Žutić and Andre Petukhov

A fridge magnet is a simple example of a non-volatile device, because it does not need power to remain stuck to the fridge door. Its magnetic state, which can be considered as stored information, is maintained indefinitely. Advances in non-volatile magnetic storage, using metal-based structures, have allowed a 1,000-fold increase in the capacity of computer hard drives over the past decade. However, this is only a small indication of the possible advances using

magnetic materials. Control of magnetism in a wider class of materials, including non-metallic nanostructures, has the potential to have an even broader impact, dramatically altering the way we process and transfer information^{1,2}.

Most electronic devices operate by manipulating the charge of the electron. However, in magnetic devices one has to look beyond the charge and focus instead on the spin of the electron and the associated magnetic moment. The spins of

a group of electrons will, in general, point in different directions (for example ‘up’ or ‘down’). A net magnetization results when more of these spins point in one direction than another. Ferromagnets such as iron have a built-in magnetization, and paramagnets develop one when a magnetic field is applied. In antiferromagnets, on the other hand, neighbouring spins point in opposite directions and there is no net magnetization. Controlling the microscopic state of a bulk magnet is a tall