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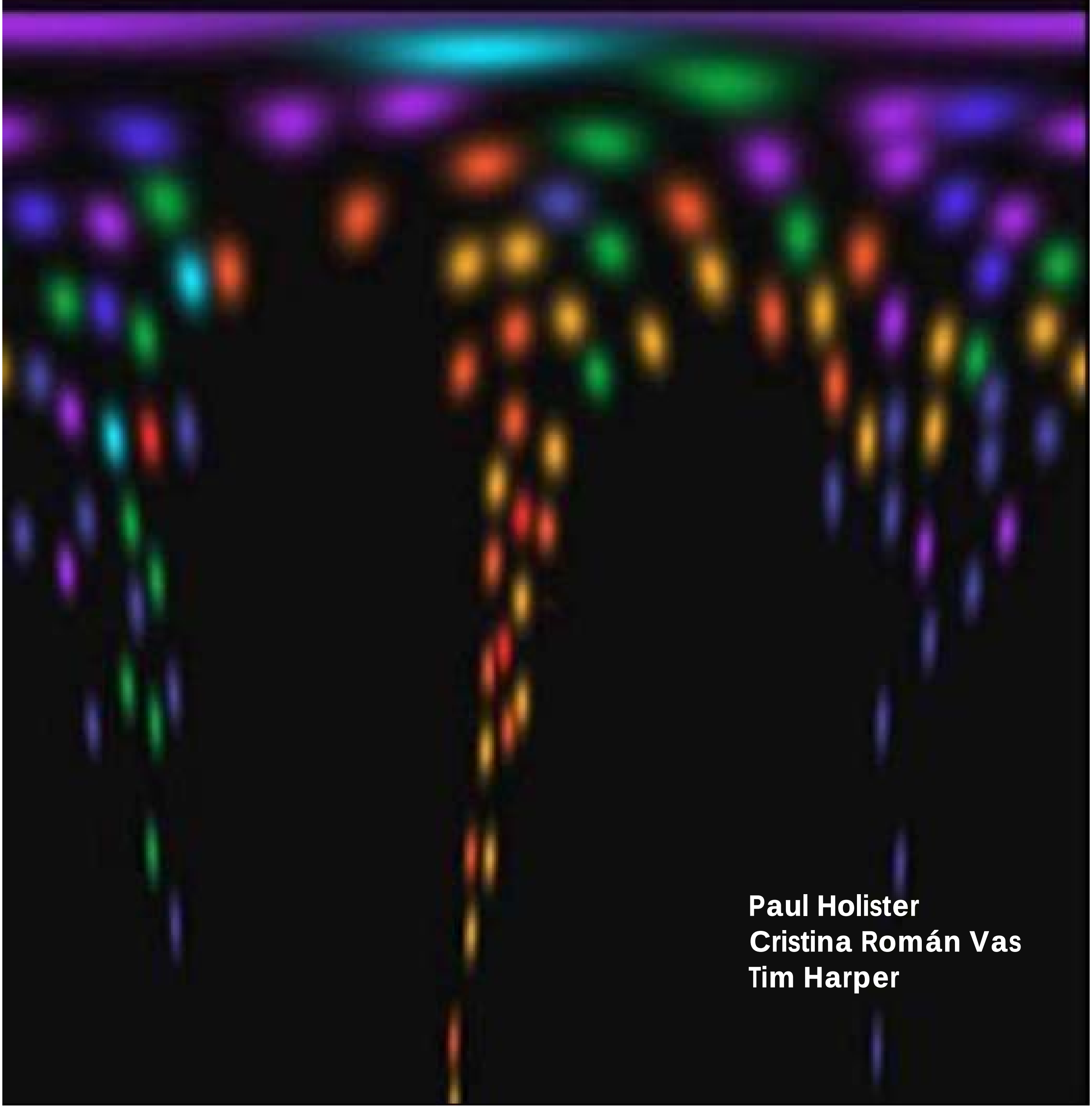
Tools

Technology White Papers
nr. 14



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Release Date: October 2003

Published by Científica

Científica, Ltd.
www.cientifica.com

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Origin of content

The free reports in this series are extracted from the technology reports that make up the Nanotechnology Opportunity Report collection and are designed to offer an introduction to the variety of technologies that fall under the nanotechnology umbrella. The full reports also include 'opportunities' sections, covering the various applications of the technology and their effects on markets, and a list describing the companies involved in the technology.

Tools

This section is effectively about our ability to view and manipulate the world on the nanoscale. It revolves primarily around microscopy techniques that already have some history and a significant and growing market, i.e. atomic force microscopy (AFM) and scanning tunneling microscopy (STM). These techniques and their variants are grouped under the term scanning probe microscopy (SPM). There are quite a few variations on these approaches, from magnetic force microscopes to AFM tips with nanotubes attached that can be functionalized (modified to perform a specific function, usually in a chemical sense). SPMs can also manipulate matter on the atomic scale. They can move individual atoms or be used to make kinks in a nanotube.

The tools market is riddled with acronyms, which are necessary given the long names of many of the tools. We will use these acronyms below but always introduce them first.

Introduction to tools

*Atomic Force Microscope Tip.
Courtesy of MikroMasch*

Most techniques can achieve nanometer precision in one or two dimensions, very few in three. What would be useful would be a way of getting elemental or preferably chemical information in three nanometer-sized dimensions. Many techniques do not achieve nanometer resolution, most others are limited on the types of material they can analyze. Older techniques, such as electron microscopy, require preparation, which can modify the sample, losing valuable information, and often need to work in a vacuum. They also generally require samples to be immobilized, though some new techniques are offering new views of living systems in real time.

Electron microscopy can almost give real-time images, though sample preparation requirements usually mean that the sample study is far removed from the real world process or system from which the sample was derived. Atomic force microscopes are too slow at acquiring data to give real-time information. What is really required is 30 frames per second, not 30 per hour. These issues are being tackled and there will no doubt be new devices springing up with new capabilities. Modification of existing devices is very active.

Scanning probe microscopes (SPMs)

Scanning probe microscopes (SPMs) are a range of imaging technologies offering atomic-level resolution. The three main kinds of SPM are the atomic force microscope (AFM), the scanning tunneling microscope (STM), and the near-field scanning optical microscope (SNOM or NSOM). These all operate by using a tip (the probe) to scan very closely across a surface, at a distance of a few tenths of a nanometer to a few nanometers. Contributing to the versatility of these devices is that they can operate in a variety of environments: in a vacuum, air or liquid. Apart from imaging, SPMs show promise in the areas of digital data storage, advanced lithography and bioanalysis.

Since the STM was invented in 1981, the number in use has roughly doubled each year. The AFM has become popular as a standard surface analysis tool, outstripping sales of STMs because it can image non-conducting samples (however, in late 2001, researchers at the Université Paris-Sud in France developed a technique for imaging diamond, an insulator, with an STM, a technique that may be applicable to other insulators). Most SPM manufacturers now offer semi-automatic AFMs for semiconductor wafer analysis.

On the R&D front, SPMs are widely used. They can be applied in the investigation of electrochemical and catalytic processes at the nanometer level. They are used to investigate and characterize new materials, whether polymers, ceramic, composites, alloys, etc. They are used to probe the electrical, magnetic and optical properties of thin films and to investigate lubrication and friction at the nanometer scale, which has particular application in the development of nanoelectromechanical systems (NEMS). They can probe the reasons for failure of electronic devices and study biological systems.

A particularly interesting use of atomic force microscopes is in dip-pen nanolithography. This uses an AFM tip, or an array of tips, and an "ink" to write lines on a surface, creating the world's smallest pen. The lines can be as narrow as 10 nm but 15 nm is more common.

Invented at Northwestern University, dip-pen nanolithography is based upon the transport of a chemically reactive material or "ink" from the tip of a conventional atomic force microscope (AFM) to the surface of interest or "paper." The process takes advantage of a tiny droplet of water that naturally forms between the AFM tip and surface of interest, and serves as the ink transport medium. Adjusting scan rate and relative humidity can control line widths.

Dip-pen nanolithography is a direct-write nanolithographic process where one can pattern and image with the same tool. These capabilities set the technique apart from almost all other nanolithographic methods and should allow one to construct "multi-ink" nanostructures and incorporate multiple chemical functionalities on a single nanochip. The method is flexible and easy to use and uses low-cost instrumentation.

Note that the method is serial in nature and this not naturally geared up to mass production. However, the use of arrays of AFM tips, as with the aforementioned storage technologies, can potentially offer a substantial degree of parallelism. Tips with holes in that can be filled with fluids are also being looked at as a way of creating patterns and prototypes with some degree of parallelism have already been developed at the Swiss Center for Electronics and Microtechnology (CSEM).

Similarly, the STM can be used in a technique similar to dip-pen lithography, by having the tip catalyze a reaction where it contacts a surface.

Near-field scanning optical microscope (SNOM or NSOM)

This microscope allows the study of the optical properties of the sample surface with a resolution better than the wavelength of the light. By scanning the optical probe at very small distances from the sample (a few nanometers) "evanescent waves" from the surface are detected by the probe. The use of evanescent waves allows bypassing of the wavelength limitation of traditional optical techniques (the traditional limit of resolution being half the wavelength in use). Resolution is in the tens of nanometers range. The SNOM can be used to image a variety of samples, including biological, as well as performing optical nanophotolithography. The main obstacle at the moment to large-scale production of these machines is manufacturing the probes reliably, the requirement for a very small hole through which the light passes being problematic.

Scanning tunneling microscope

Invented in 1981 by Heinrich Rohrer and Gerd Karl Binnig (who were awarded the Nobel Prize five years later) the STM works by detecting small currents flowing between the microscope tip and the sample being observed (the current flows because of quantum mechanical tunneling). It can be used to image and manipulate individual atoms.

Atomic force microscope

Invented in 1986, the atomic force microscope (AFM) has similar capabilities to the scanning tunneling microscope. Instead of detecting a tunneling current, it detects the force between the tip and the sample under observation. It has a tiny probe on the end of a cantilever (like a springboard), which travels over the surface of the sample and is deflected by the variations in the surface topography (shape, essentially), causing the cantilever to bend. The bending of the cantilever is detected by measuring the deflection of a laser beam produced by a laser diode. The simplest and most common use of an AFM is to map the topography of the sample surface, however it has a wide range of applications including imaging at a nanometer scale the friction and adhesion properties of the surface, as well as mapping the electrostatic or magnetic variations in the sample. For the latter two applications there are AFM variants called the magnetic force microscope (MFM) and the electrostatic force microscope (EFM). Depending on the application and the conditions of operation, the AFM can achieve true atomic resolution or on the order of nanometers. It can work well in vacuum, air or in liquid and can be used for very different samples: semiconducting, conducting, biological, etc. Apart from imaging, it can be used for sample manipulation at atomic or nanometer scale, as well as for nanolithographic processes.

Significant work has been done on attaching carbon nanotubes and other materials to AFM tips. Carbon nanotube tips show promise for inspection of semiconductors and are especially good at imaging of surfaces with a strong 3D aspect (i.e. significant vertical variation). Carbon nanotubes can also be "functionalized" to have specific chemical affinities. Other nanotubes, such as those made from tungsten compounds or boron nitride, have greater stiffness than carbon nanotubes and may prove useful in creating nanostructures such as trenches. Silicon "whiskers" can also be grown on AFM tips.

Note that as AFM manufacturing is a mature industry, there is a wide variety of companies providing cantilevers, accessories, add-ons, software etc.

Electrostatic force microscope (EFM)

The EFM uses a metal-coated tip to measure the electrostatic interaction between tip and sample. This allows imaging of the electrostatic properties of the sample. It can be used to characterize electronic devices at a nanometer scale, for example at the development stage or for failure control processes.

Magnetic force microscope (MFM)

The MFM uses a ferromagnetic probe to pick up magnetic fields close to the specimen's surface. It is particularly useful for imaging magnetic surfaces such as those in magnetic storage media.

Field-ion microscope (FIM)

Field ion microscopy (FIM) was introduced in 1951 by Dr. Erwin Mueller, who had previously invented the field emission microscope (FEM) in 1936. At the time of its introduction, the FIM was the only experimental method capable of atomic resolution, and remained such for quite some time. The technique has been largely supplanted by techniques such as transmission electron microscopy and atomic force microscopy.

FIM uses a sharp tip, which is placed in a vacuum chamber and pointed towards a fluorescent screen. An imaging gas is released into the chamber and a high electric field around the tip is created. As the image gas atoms approach the tip they are ionized and accelerated towards the fluorescent screen, where they form an image representative of the surface of the tip.

Electron microscopy

Early electron microscopes were first built as long ago as 1934, with the first commercially-available machine appearing in Germany in 1939. The key to their value over earlier forms of microscopy was that electrons have a much shorter wavelength than visible light, and therefore higher resolution can be achieved. In all electron microscopes, a beam of electrons is accelerated towards a sample, and focused down to a very small spot, usually of the order of a few nanometers. This electron beam is scanned across the sample and a picture is built up of either the secondary electrons generated by the incident beam (scanning electron microscope—SEM) or transmitted through the sample (transmission electron microscope—TEM).

A major drawback of either technique is that, to achieve high resolution, the sample must be placed in a vacuum, and requires several preparation steps.

TEM has sub-nanometer resolution, but requires the sample to be thinned to a point where it becomes electron transparent—usually around 100 nm. Producing these thin slivers of material divorces the imaging process from the real world sample, and sample preparation can take weeks. Current instruments can achieve 0.1 nm resolution, and a wide range of accessories is available to allow the acquisition of chemical or crystallographic information on the nanometer scale.

A far more rapid turnaround can be achieved by SEM, the main requirement being that the sample is made conducting. This is usually achieved by coating the sample with a very thin layer of gold, which may, in itself, introduce nanometer scale artifacts into the sample. Current state-of-the-art SEMs can achieve resolutions as good as 1 nm. Uncoated samples can be imaged by either using a field-emission-based electron column, allowing low accelerating voltages to be used and avoiding sample charging, or by introducing gas into the microscope chamber. Both of these methods degrade imaging resolution. Elemental information can be acquired, although due to the physical process involved resolution of less than one micron is difficult to achieve.

The 50-year history of electron microscopy has built up a huge body of knowledge on the properties and manipulation of electron beams, allowing major advances in electron beam lithography. Most SEMs can be converted from imaging to electron beam lithography instruments by the addition of suitable hardware and software.

Focused ion beam milling (FIB)

FIB instruments use a finely-focused beam of ions, usually gallium, accelerated to between 30 and 50 KeV (thousand electron volts), to physically remove material by a process known as sputtering. This is a direct write method of fabrication whereby each structure must be individually etched in the instrument (as opposed to conventional photolithographic techniques where a mask may be produced in one instrument and processing carried out in a variety of instruments). A variety of gases can be added to the vacuum system in order to selectively enhance the milling of one element over another.

As current instruments can achieve beam diameters of less than 5 nm, FIB is a useful technique for the controlled removal of material with high accuracy in all three dimensions. The major drawback of FIB in microtechnology is its slow rate of material removal, especially at small spot sizes. Given the small material volumes required to be removed in the nanoscale, this may be less of a problem. The chief obstacle to the use of FIB for large-scale production is that each structure must be individually created within the FIB instrument, leading to serial rather than parallel production though work has been done on using scanning ion beams with a mask and resist, similar to the use of electron beams in electron projection lithography.

While commercial instruments are gallium-based and primarily used for semiconductor failure analysis, academic groups have been working on much higher voltages and a wider range of ion species.

New interferometry techniques

Interferometry, which is using interference of light beams to measure small changes in distance, has been around for a long time but recent developments offer much improved resolution. A group at the University of Stuttgart reported late 2001 on a technique that gets around the half-wavelength limit that bedevils several optical technologies (see the Near-Field Scanning Optical Microscope) by sending a laser beam in at an angle into a narrow gap between two parallel mirrors, one fixed and one movable. The beam separates into several "modes"—waves that bounce off the mirrors a different number of times as they travel down the long gap. The modes recombine to produce an output beam whose intensity depends on the exact distance between the mirrors. The more reflections that occur, the smaller the shifts of the movable mirror required to change output intensity. The researchers were able to detect movements as small as one-ninth of a wavelength, roughly 70 nanometers, but think a thousandth of a wavelength or smaller might be achievable if the mirrors could be made sufficiently flat.

Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance (NMR) detects the response of nuclei to a magnetic field and radio waves. This response (the resonation) varies according to the cumulative effect of the spins of protons and neutrons in the nucleus, the net of which may be zero spin for the nucleus, meaning NMR will not produce a response. Since the applied fields normally affect quite a large sample of matter, the resulting resonation is from a collection of nuclei, including information on their neighborhood, and quite sophisticated techniques are required to get useful information out of this. Ultimately, though, the information provided comes from the nuclei of individual atoms so this technique does offer information at the atomic level.

Magnetic resonance imaging (MRI) uses NMR to map the density of an atom (usually hydrogen) in a sample and thus produce an image. It can be used on living tissue, and has been used for many years now in medical scanners, most notably in brain imaging. NMR generally gives a lower-resolution structure than X-ray crystallography, but it does not require crystallization.

Positron annihilation

In this technique positrons are implanted into a material where they annihilate with one of the electrons of the medium, producing photons. Measurements of the angular and energy distributions of these photons lead to information about the material. The presence of defects in a solid produces annihilation characteristics that provide atomic-scale signatures of the defects. Such information is not accessible from traditional techniques such as electron microscopy.

The technique can detect void-type defects (i.e. holes) in polymers, metals, ceramics and glasses, and has been used to detect nanometer-sized holes in paint surfaces.

Surface plasmon resonance

This is a phenomenon that occurs when light is reflected off thin metal films and a small amount interacts with electrons in the film, reducing the light intensity. The refractive index of the materials sandwiching the film dictates the angle at which the light reduction (essentially a shadow) occurs. Substances that interact with one of the refractive surfaces can change the refractive index and thus the direction in which the shadow is cast, allowing imaging of the interaction. The interaction of biomolecules can be detected in real time, offering applications largely for observing biological systems in action on a very small scale, but also with potential for biosensors. Surface plasmons in general were the subject of some interesting general research in late 2002 and early 2003. There is still a lot to be learned in this field, and consuquences for imaging systems are probably to be expected.