

transport (see the discussion below). They also perform a thermal analysis, which shows that, despite the high local fields and current densities in the electrodes, the temperature in the 'on' state is only a few degrees above that in the 'off' state, due to excellent heat conduction at the nanoscale. This might explain why the dielectric breakdown that leads to the 'on' state is reversible. The ability to turn the electrode 'on' or 'off' with an applied field is a rather attractive feature because it reduces the chances of inadvertent current leakage.

The paper also leaves us with an intriguing question that deserves further research: what are the charge carriers in the electrodes? The authors argue against ionic conduction because they do not observe any accumulation and depletion of salt at the opposite sides of the 200-nm nanolayers, called concentration

polarization. However, it is hard to see how electronic conduction could occur, because this would involve local redox reactions at the solution/glass interface, and such reactions would still cause accumulation of reaction products at the liquid/nanolayer interfaces. Conduction through glass (in, for example, glass pH electrodes) has been studied for many years and has been attributed to proton or sodium ion transport^{4,5}, amongst others. If these ions are the charge carriers in nanoscale liquid glass electrodes, they would be injectors of specific ions rather than of electrons. Redox reactions would be avoided and a range of interesting new possibilities would be opened up.

We expect that laser micromachining will be predominantly a research and prototyping tool, because of its one-off character and

the high cost of the equipment involved. However, the work by Hunt and colleagues¹ shows how well it can serve that purpose and the unprecedented devices that can result. □

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INTERFACES

AFM extends its reach

A commercial atomic force microscope can be used to image solid surfaces in liquids and measure interfacial energies with atomic resolution.

Andreas Ruediger and Federico Rosei

Surfaces and interfaces exhibit a variety of fascinating properties that can be harnessed for applications such as catalysis, electronics and energy conversion¹. Solid/liquid interfaces are of particular significance and are critical in elementary phenomena as diverse as wettability and crystal growth. The properties of such interfaces can be characterized by their interface energy, which is defined as the sum of the two surface energies, minus the work of adhesion required to separate them. Conventional experimental approaches to determine the interface energy, such as contact-angle measurements, are inherently macroscopic and average over large areas, thereby neglecting local effects due to the structure of the surface or interface at the nanoscale². However, because most of the atoms in a nanostructure reside at its surface, there is a pressing need for experimental techniques that are capable of measuring surface structures and interface energies with high spatial resolution.

Scanning probe microscopy³ comprises a suite of experimental techniques based on the interaction between a sharp tip and a surface, which can provide morphological images of substrates. In atomic force microscopy⁴, the interaction between the tip and the surface is determined by a combination of forces (mainly van der Waals, electrostatic and

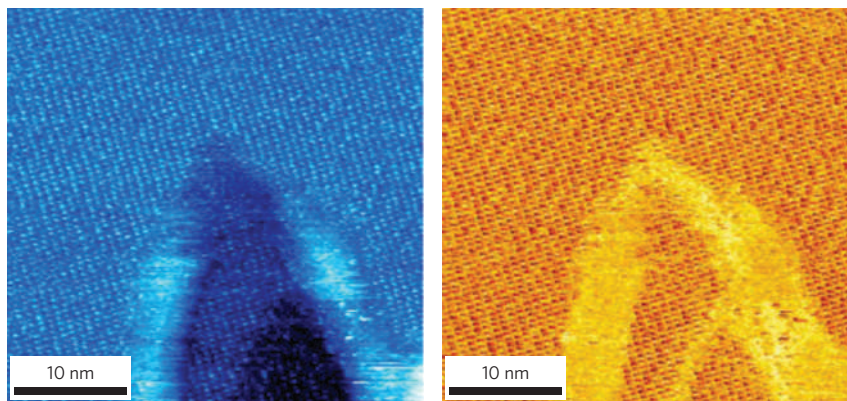


Figure 1 | Mapping solid–liquid adhesion energy with an AFM. Small-amplitude-modulation atomic force microscopy images of calcite (CaCO_3) in ultrapure water. A topographic image is shown in blue and a phase image, which maps the phase of the cantilever oscillation during a scan, is shown in yellow. (Figure courtesy of F. Stellacci).

solvation forces), which decay as a power law with respect to distance. The atomic force microscope (AFM) has undergone a number of major advances in recent years: for example, it was recently used to image submolecular features in individual molecules⁵ and to measure the force required to move a single atom⁶.

Writing in *Nature Nanotechnology*, Kislun Voitchovsky of the Massachusetts Institute of Technology (MIT) and co-workers

now report how a commercial AFM can be used to measure relative interface energies at solid/liquid interfaces⁷. The approach also allows atomically resolved images of various surfaces immersed in liquids, including mica and calcite surfaces in water, to be obtained (Fig. 1); such high resolution has been previously observed only in a handful of cases at the solid/liquid interface.

The experiments of Voitchovsky and colleagues — who are based at MIT, Oxford,

Trieste and Lausanne — are carried out entirely in liquid and therefore involve two liquid/surface interfaces: the sample/liquid interface of the system under investigation and the tip/liquid interface, which can be considered to be independent of the tip position. The experimental key to obtaining atomic resolution is to operate the AFM dynamically with a cantilever that vibrates with small amplitude. Through a series of careful measurements, the authors establish the exact parameters necessary for high-resolution imaging⁸. They find that the optimal conditions for imaging occur when the tip oscillates as close as possible to the substrate without significantly interacting with it, and a simple theoretical model is used to describe this imaging mechanism.

The model assumes that, as the tip oscillates, the tip/liquid interface and the sample/liquid interface merge, coalescing into a single interfacial liquid layer, before returning to the original separate interfaces. This process is considered to be non-adiabatic — the liquid molecules do not have enough time to return to their equilibrium position during an oscillation — and the energy dissipated with every oscillation is directly related to the work of adhesion (which, in turn, is related to the interfacial energy) of both interfaces. The energy dissipated can be measured with the AFM, and work-of-

adhesion maps can therefore be obtained with nanoscale resolution.

The work-of-adhesion values obtained using this approach were also compared to those calculated from macroscopic contact-angle measurements. Good agreement was found, yet with a systematic error between absolute values. This error is thought to arise primarily from different energy-dissipation mechanisms that were neglected in the tip-oscillation model. However, the authors develop a calibration procedure that limits the error to no more than 5%.

The technical developments of Voïtchovsky and colleagues provide a number of intriguing opportunities for application. Their approach could, for example, be used to help understand crystal growth, as it should allow the early stages of precipitation from the solution phase (including nucleation) to be visualized with high resolution, while simultaneously measuring variations in the interfacial energy. The relatively simple experimental requirements — a commercial AFM with a liquid-cell attachment — also mean that the technique could be readily used by a range of researchers to systematically study various combinations of interfaces and solvents.

To bridge the gap between nanoscale and macroscopic objects, the next step will be to consider topographic effects as opposed to

atomically flat substrates. Resolution could also perhaps be improved by using nonlinear forces related to higher harmonics⁹. Finally, simultaneous scanning in the *z* direction should allow the whole three-dimensional interfacial space to be examined, as was recently demonstrated in the water/mica interface¹⁰. The dynamic lateral ordering in the first monolayer of water could then also be observed. □

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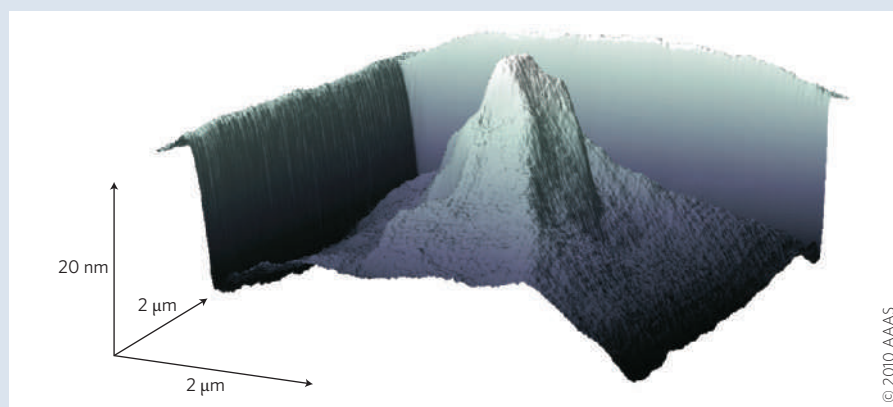
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NANOFABRICATION

Hot tips for surface patterning

The semiconductor industry uses masks to write patterns onto substrates at many stages during device fabrication. Masks are commonly made from organic resist materials because they are amenable to patterning. However, standard optical and electron beam lithography techniques struggle to produce mask feature sizes below 30 nm. Now, Armin Knoll and colleagues at IBM Research centres in Zurich, San Jose and Yorktown Heights have used a scanning probe to pattern resists to a resolution of 15 nm at high speeds and in three dimensions (*Science* **328**, 732–735; 2010).

The method involves applying a controlled amount of heat and pressure to a glassy organic resist through a scanning probe tip, overcoming the weak hydrogen bonds that bind the resist molecules and causing the resist to evaporate. Previous 'heated tip' methods involved breaking covalent bonds or causing chemical changes, which made them slow and also led to contamination of the tip. The new approach allows a resolution



of 15 nm to be achieved at speeds comparable to electron beam lithography, which are sufficient for rapid prototyping. Higher speeds could be reached by using many scanning probes simultaneously.

The technique can also produce three-dimensional patterns by successively scanning over the same area of resist,

removing varying depths with each scan. The IBM team used this approach to construct a 25-nm-high replica of the Swiss mountain, the Matterhorn. This shape (pictured) was subsequently etched into a silicon wafer.

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