Media communiqué

Materials Science & Technology

Duebendorf, 15th May 2007

Silicon nanowires for Raman spectroscopy – molecular manipulation with unheard of precision!

Measuring internal stresses with the perfect tip

We expect them as a matter of course, as self-evident as sunshine in summer – more powerful computers, cell phones with yet more functions, even smaller MP3 players, and so on. At the heart of each of these high tech devices sits a silicon chip bearing minute electronic circuits. To monitor the quality of such chips, optical methods such as Raman spectroscopy are used. Empa materials expert Johann Michler and his team have now managed to make significant improvements to this spectroscopic technique. With colleagues from the Max Planck Institute for Microstructure Physics in Halle, Germany, the Empa researchers constructed probe tips out of silicon nanowires which improve the precision of the Raman method by a factor of up to a hundred. This allows changes at the molecular level – such as those on a microchip - to be observed.

Studying the properties of materials at the nanometer level is a speciality of the new Empa Mechanics of Materials and Nanostructures Laboratory in Thun. Johann Michler and his team are conducting research into the inner structure of solids with the help of so-called tip enhanced Raman spectroscopy (TERS). A laser beam scans the surface of the sample and causes the molecules to oscillate. In doing so, they absorb some of the light, reradiating it later in a phenomenon known as «Raman scattering». This effect is unique for many substances, a sort of optical fingerprint, and it allows scientists to infer not just the composition of a sample, but also whether it contains crystal faults or internal stresses.

Locally enhanced laser spot makes molecules visible

Until recently researchers such as Michler and his colleague Silke Christiansen of the Max Planck Institute in Halle were, however, confronted with a problem. In order to use the spectroscopic technique to detect mechanical stresses in minute components the laser spot needed to be locally enhanced. This required a metallic tip, ideally manufactured to exactly the right size and shape with nanometer accuracy, something which to date was not possible technically. The technique was therefore not sensitive enough to allow quality control of materials on the nanometer scale and to uncover minute structural faults.

For decades, scientists have faced the problem of how to make molecules visible with the help of laser beams. The wavelengths of the light emitted by lasers are still much longer than the nanometer scale dimensions of molecules, which therefore cannot be «seen» – resolved, in scientific jargon – by the laser light. One way to «trick» the visible light waves was discovered in 1974 by the American chemist Martin Fleischmann, the same scientist who, fifteen years later, would claim to have discovered cold fusion in the laboratory. While his cold fusion experiments could not be reproduced by other researchers (and are today considered to be erroneous), his optical experiments have revolutionized several scientific fields including Raman spectroscopy.

Fleischmann discovered that a rounded tip coated with gold or silver can be used to efficiently couple laser light into molecules or crystals. Doing so makes the Raman technique significantly more sensitive, theoretically enabling individual molecules to be identified. In practice, to date the factor limiting the resolution of the method has been the fineness of the tip which can be achieved. The sputtered gold surface of the tips tip takes on randomly different shapes, so that each one is slightly different in shape and size. «These tips look like the Matterhorn under the microscope», says Michler. To be able to follow surface features with a spatial resolution in the nanometer range – such as for example how microelectronic components change over time – requires that the tips must be identical to the nanometer. Only then the measurements are comparable.

Silicon nanowires with identical gold heads

Now Michler and Christiansen have developed a new method of creating even finer Raman tips. They grow silicon nanowires with gold heads on a silicon substrate, the nanowires growing like blades of grass on a lawn. In contrast to grass, however, they are just a few micrometers long, with diameters selectable between 25 to 500 nanometers. The most important feature is that all the nanowires have identical, perfectly round gold tips. No trace of the Matterhorn now, more a case of the cupola on the Federal Parliament building in Bern.

The nanowires are then welded onto a holder in an electron microscope. «This allows us to see the wires and we can guide them precisely to where we want to locate them, and then fix them in place», explains Stephan Fahlbusch, the nanotools specialist in Michler's team. He and his colleague Samuel Hoffmann use a joystick to move the holder to the vicinity of one of the nanowires. A quick twitch of the joystick and the wire adheres to the tip, where it is welded in place using the electron beam. Now Fahlbusch can use the tip for nano-Raman spectroscopy experiments. The sensitivity of the new method is demonstrated by the colleagues in Halle, where the tip was scanned over a layer of malachite green. Although only single molecules of the dye were present on the substrate, the equipment produced a definite Raman signal. This means that the resolution of the technique is high enough to measure changes in the internal mechanical stresses of semiconductor materials, for example. This is important because it indicates the presence of defects or material fatigue.

Automization – the next step

Michler's method of producing nanotips for Raman spectroscopy applications represents enormous progress, above all for the EU-Project Nanohand, in which Empa researchers, together with partners from France, Germany, and Switzerland, have been involved since 2006. The aim is to construct a nanorobot for the semiconductor industry which will be capable of handling miniaturized samples on the platform of an electron microscope and producing tips without human intervention. Automated production, with its associated cost reductions, will extend the range of applications of the nanotips, for example to the chemical analysis field. This might allow forensic science or hospital hygiene to benefit from the potential offered by nano-manipulation, by allowing for example a conviction to be obtained by the discovery of a single cocaine molecule on the jacket of a suspect or the identification of a single lethal bacterium which triggers a pandemic-avoiding quarantine.

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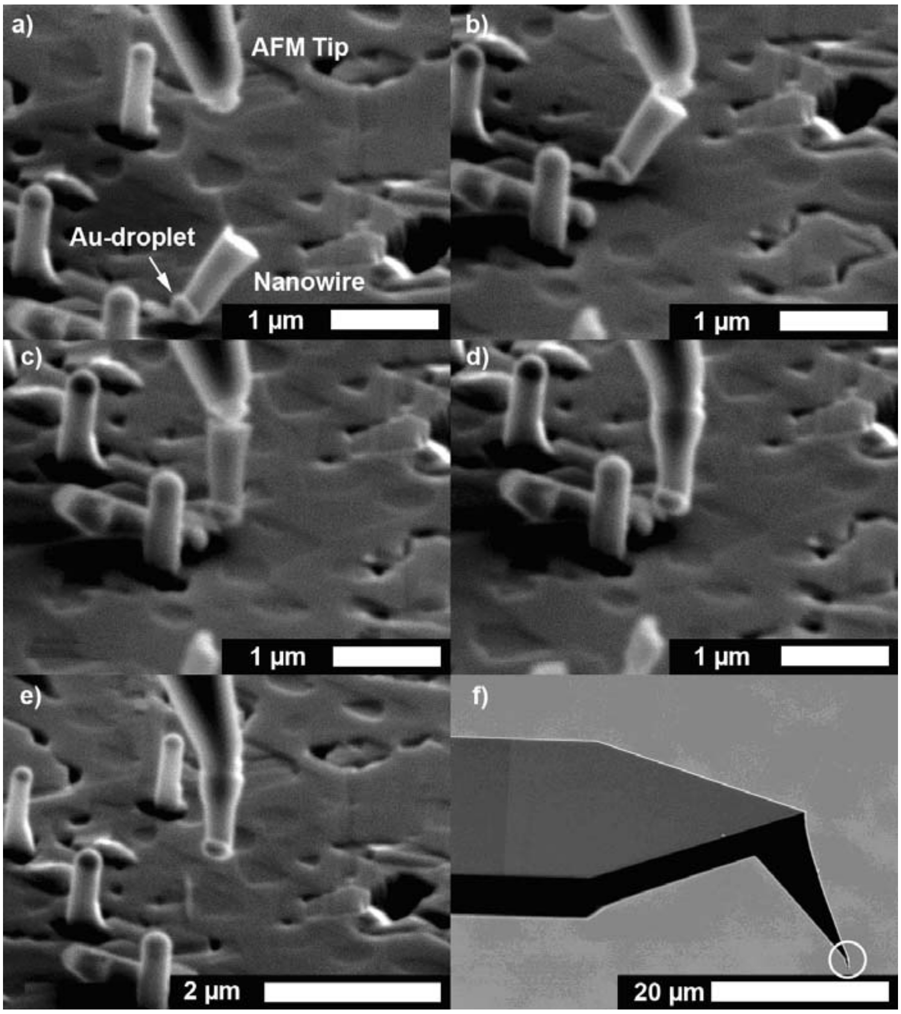

A sequence of images showing the steps necessary to create a nanotip for Raman spectroscopy applications: a) a nanowire is broken off from the silicon "lawn" and turned on its head, b) the still-unfinished tip of the spectroscope contacts the nanowires, c) the tip maneuvers the nanowire into a vertical position, d) the tip and nanowire are welded together by an electron beam, e) the finished nanotip is removed from the microscope, f) the holder with the finished tip, ready to be used for Raman spectroscopy measurements.

Images are available in electronic form from Sabine Borngraeber (sabine.borngraeber@empa.ch) or Remigius Nideroest (remigius.nideroest@empa.ch).