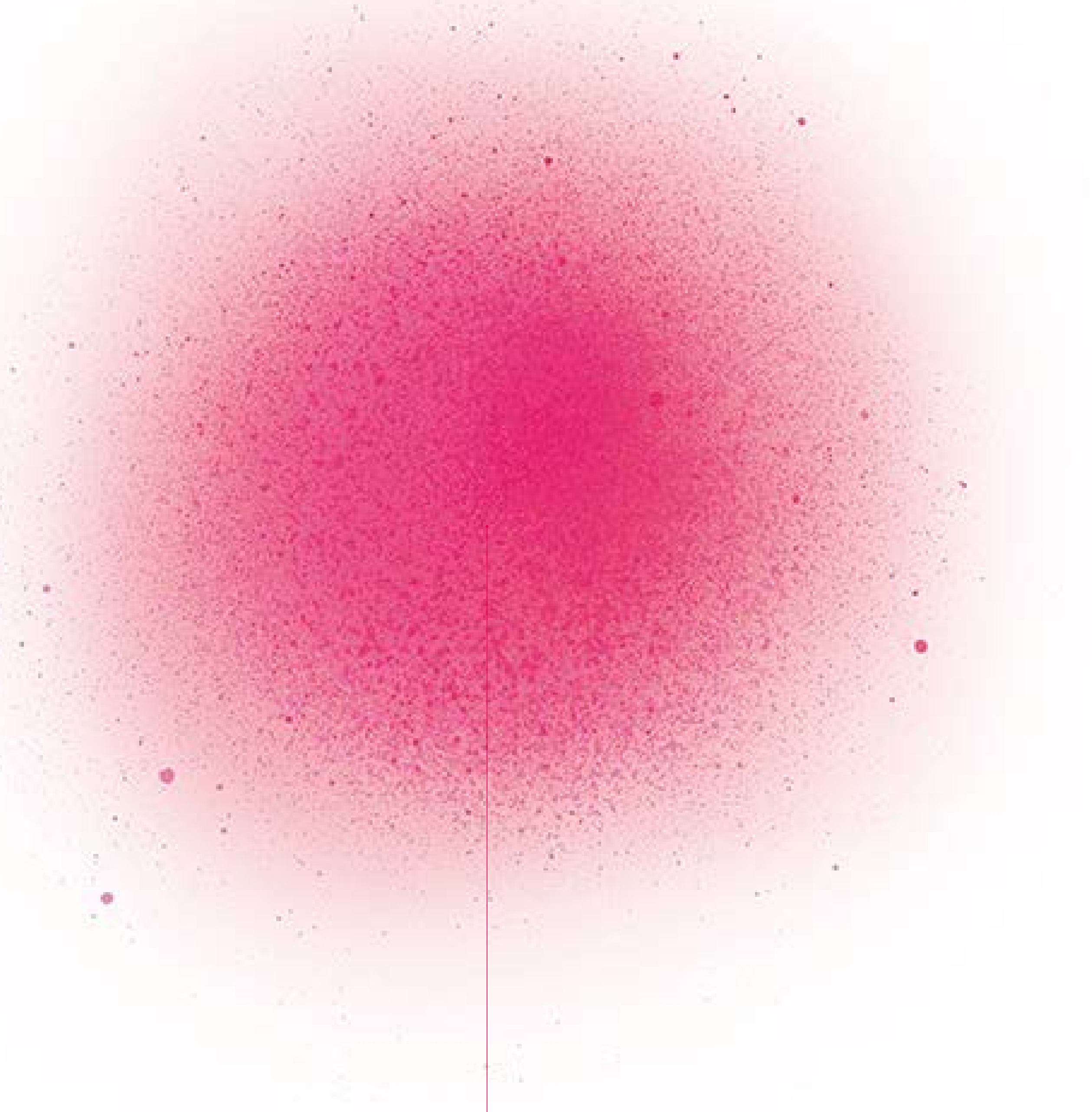


up to

90%

transmittance

bendable

a few tens of
nanometers thick

Nano Sprays **with a Spark**

Why complicate something so simple? This was the question posed by researchers at TUM's Institute for Nanoelectronics. The group led by Prof. Paolo Lugli wanted to replace complex and expensive coating methods using exotic materials with common spraying and inkjet printing processes. With impressive results. The list of industrial applications that can use these innovative methods is long and growing all the time.

Picture credit: ediundsepp

Link
www.nano.ei.tum.de

Nano-Sprays mit Pfiff

Neu entdeckte Materialien versprechen neue Möglichkeiten: Nanoröhrchen aus Kohlenstoff, Graphen, leitfähige Polymere oder Silber-Nanodrähte können bei der Entwicklung einer Vielzahl elektronischer Produkte und Sensoren innovative Wege eröffnen. Prof. Paolo Lugli und seine Mitarbeiter am Lehrstuhl für Nanoelektronik der TUM haben dafür in den letzten Jahren die Sprühbeschichtung perfektioniert. Dabei werden mit Sprühköpfen hauchdünne Schichten auf die verschiedensten Oberflächen aufgetragen. Dies ist weitaus billiger und schneller als bisherige Verfahren wie Sputtering oder Epitaxie. Auch die Methode des Tintenstrahl-Druckens nutzen die Forscher, beispielsweise um die dazugehörigen elektronische Schaltungen schnell und billig herzustellen.

Intelligente Anwendungen für Alltag und Labor

Anwendungen gibt es viele, und täglich kommen neue Ideen dazu: Gassensoren sollen bald die Luft in Innenräumen überwachen oder messen, wann Fleisch verdorben ist; Sensoren für die Ionenkonzentration in Flüssigkeiten können ganze Labors ersetzen, die Forschung in der Pharmabranche erleichtern oder unser Trinkwasser überwachen. Andere Sensoren werden vielleicht bald in Küchenherden, Kühlschränken oder Waschmaschinen Temperatur und entstehende Gase detektieren. Transparente Schichten, die sich bei Anlegen einer Spannung erhitzen, könnten Windschutzscheiben abtauen und Windkraftanlagen eisfrei halten. Und in Zukunft könnte man dreidimensionale Objekte, die in 3D-Druckern hergestellt werden, mit aufgesprühten funktionalen Schichten kombinieren und auf diese Weise intelligent machen. *Brigitte Röthlein*

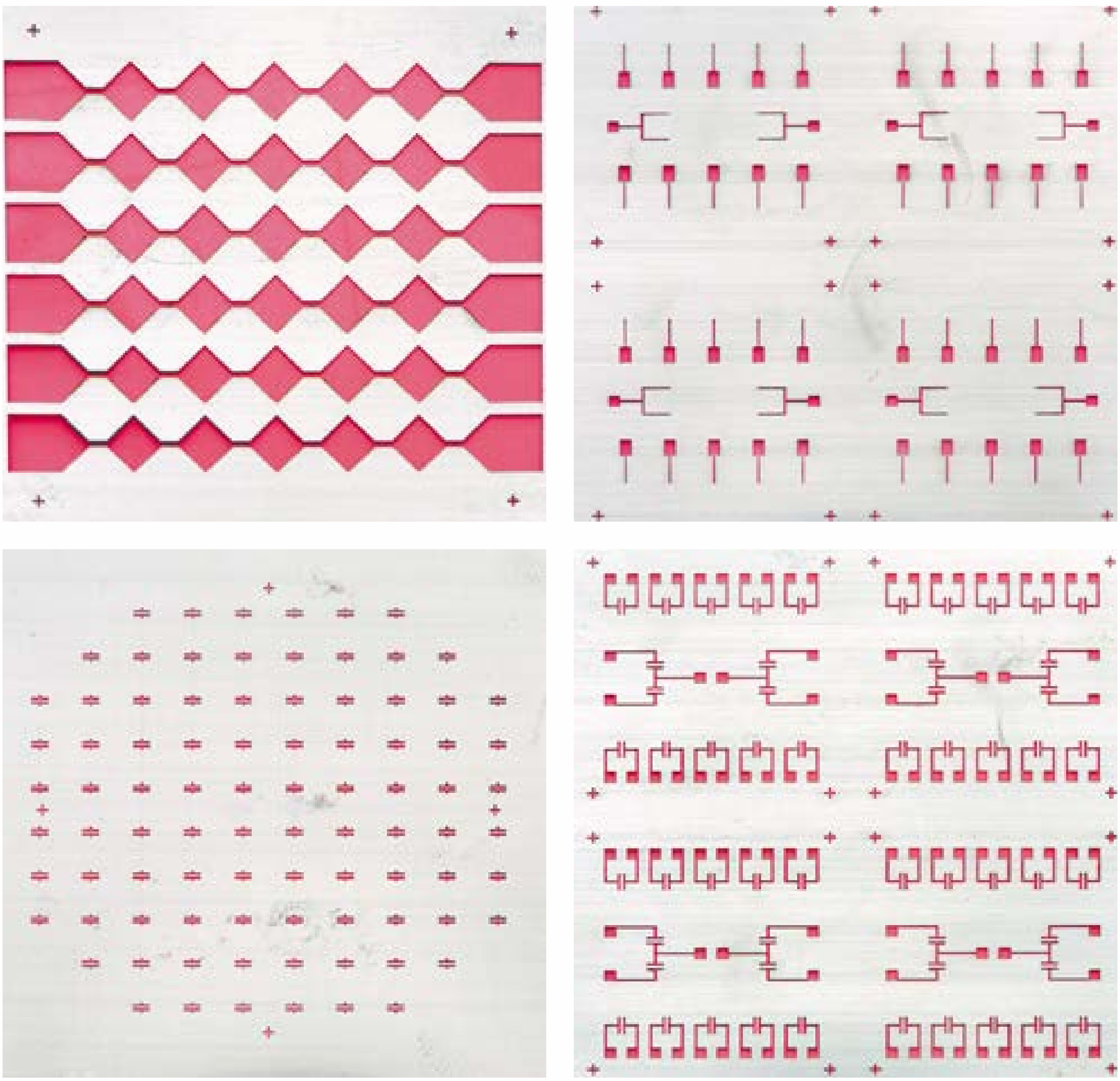
Science is still full of surprises. Numerous new materials have been discovered in recent years: carbon nanotubes, graphene, metal nanowires and conductive polymers. Methods have been developed to produce these exotic substances in greater quantities and with a sufficiently high level of purity, but researchers are still racking their brains about what they can actually do with them. “This is a rapidly growing field of technology,” comments Paolo Lugli, Chair of Nanoelectronics at TUM. He and his team are developing methods to apply ultra-thin layers of the materials onto a variety of substrates, thus making them useful for a wide spectrum of applications. At the forefront are spray deposition and inkjet printing. While already an industrial standard for many applications, these methods are now making their way into the world of electronics.

The arrival of the unbreakable cellphone

One example is transparent electrodes, found in touchscreens, television flatscreens and solar cells. Up to now, these have been made of indium tin oxide (ITO). This is an expensive and brittle material that tears easily when applied to flexible films, which means that the electrodes lose some of their electrical conductivity. Carbon nanotubes (CNT) provide a solution to this problem.

They form a dense mesh of conductive tubes when deposited on a surface. When bent, the mesh moves elastically, but does not tear. This opens the door to the development of cellphones with bendable, shatter-proof touchscreens. Another plus is that carbon is an abundant material, unlike the heavy metal indium, which occurs in the Earth’s crust as rarely as silver or mercury. “Electrodes made of CNT are 80 percent transparent,” explains Lugli, “which makes them highly suitable for optical applications.” His colleague Dr. Alaa Abdellah has developed a spray coating process that allows ultra-thin and very even layers to be applied over both small and large surfaces. “We have been working on this for over six years, so we have a lot of experience at this stage,” he affirms. “First of all, you need good spray heads, and then the right interplay between the ink, the spray parameters and the distribution.” Over this time, the researchers under Lugli and Abdellah have learned a number of tricks to help them achieve good results. They know how to produce the most homogeneous inks from exotic substances, how to make them adhere to the substrate, how to remove unwanted chemicals afterwards and how to achieve a perfectly even sprayed film. “All of this trial and development work required a great many bachelor’s, master’s and doctoral theses,” confirms Paolo Lugli. “And we are still a long way from the finish line. New challenges are always popping up for which we have to find clever solutions.”

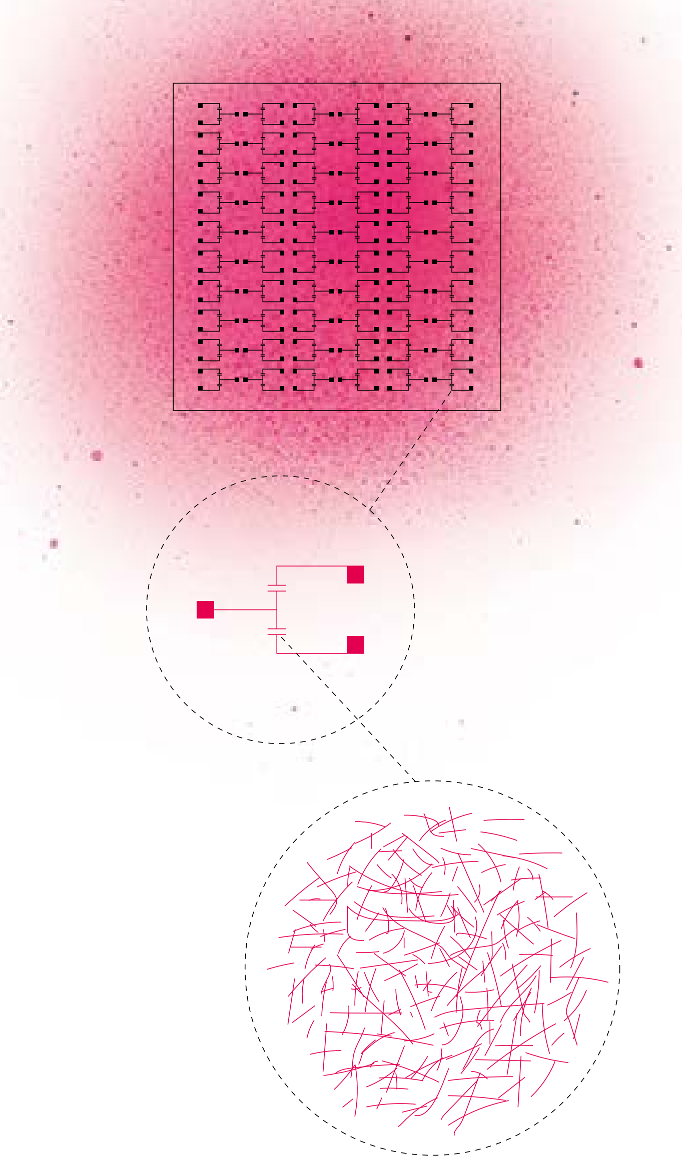
For instance, there is the question of how to distinguish between gases using the CNT layers. The researchers have already proven that the carbon nanotubes, deposited on a foil, are able to detect gas molecules. The gas molecules attach themselves to the nanotubes and alter the conductivity of the layer. This change can be measured and used to determine the concentration of molecules in the environment. The challenge now is to detect the gases on a selective basis, for example distinguishing carbon dioxide (CO_2) from ammonia (NH_3), carbon monoxide (CO) or nitrogen oxides (NO_x). For each of these gases, there is huge demand for a low-cost sensor that can be mass-produced. These sensors could be used, for instance, to monitor CO_2 levels in indoor spaces, to detect NH_3 and thus spoilage in packaged meat, and to protect health and safety by monitoring toxic CO and NO_x levels. “We are on the brink of making the CNT films selective,” promises Lugli. “Right now we are looking at functionalizing the layers with nanoparticles, using palladium or gold for example.” These elements react with the individual gases in different ways and therefore alter the conductivity of the layer in a distinctive way. “If we are successful, then before long, every classroom, lecture hall or conference room could be equipped with a CO_2 meter to indicate when the room requires urgent ventilation. Air conditioning units could also be fitted with such sensors.” Besides gas concentrations, the nanolayers could also measure temperature. Manufacturers of household goods are already considering such applications in stovetops, washing machines and refrigerators. ▷



Picture credits: Filser

It all begins with simple shapes stamped onto templates. The researchers use these to see whether the exotic materials that they spray onto films will adhere properly and distribute evenly without running off. Later, when they are working on industrial applications, they must ensure that the spray coating has been applied precisely. This is the only way to ensure that the delicate sensor structures function correctly.

Integrated circuits by inkjet
The TUM researchers are by no means limiting their work to gas-related applications. They also have some interesting plans for liquids. For example, they have succeeded in covering CNT sensor fields with membranes that selectively allow only specific ions such as chlorine, magnesium or calcium to pass through. These in turn alter the conductivity, so their concentration can be measured with great accuracy using an electronic circuit. The group has submitted a patent application for its array of ion-sensitive sensors, rather like electronic noses analyzing different smells. "We tested the sensors on various mineral waters and were delighted to find that we were able to distinguish between them," reports Lugli.
They are hoping to develop this idea further to create a "lab on a chip" capable of capturing and measuring multiple parameters in parallel on a miniature scale. This could be used to monitor drinking water quality, for example, or for the chemical analysis of blood and other organic liquids. A particularly interesting project is under way in cooperation with the University of Alberta in Canada. The researchers want to place living cells directly onto the sensors in the hope of being able to study the function of the cell membrane. How quickly are calcium, potassium or sodium absorbed or released through their ion channels, and under what conditions do the cells become healthy or diseased? "Finding answers to these questions is of huge importance for the development of new drugs," points out Lugli.
While the sensors are highly intelligent, they cannot do it all. Some form of electronic device is needed to analyze the measurements, read them out or send them to a cellphone. Abdellah and his team are working on a fast and cost-effective way of producing such circuits using inkjet printing. "The ink we use is made from silver particles, which we print onto photographic paper or plastic foils and then sinter with a UV flash lamp," explains the engineer. "We can then add standard electronic components, just like on a conventional printed circuit board." The devices thus produced may be considerably larger than current microelectronic chips, but they ▷



When viewed under the microscope we can see that the structures of the sensors (center) are composed of extremely fine carbon nanotubes (bottom) that form a dense mesh when deposited onto a surface. With their spray method, the TUM researchers can layer them onto films in large quantities (top).

Picture credit: Filser/graphics: ediundsepp

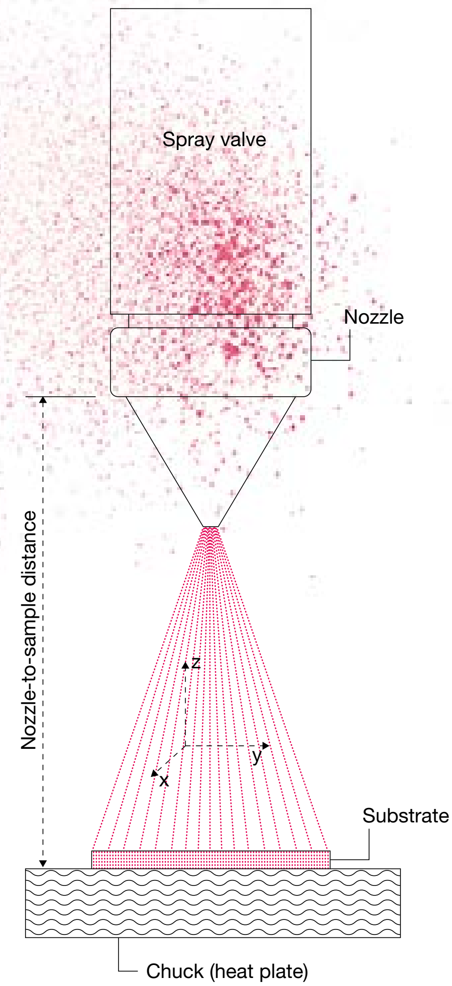
Patience and care are needed when developing the delicate structures. The TUM researchers use inkjet printing to manufacture the electronic circuits for the sensors. Here, Dr. Alaa Abdellah uses a microscope to connect one of the tiny transistors to a carbon-nanotube-coated sensor in order to test its electrical properties.

can be manufactured and tested quickly and at low cost. In everyday life, miniaturization is not always the most important driver; often it's about producing devices cheaply and on a large scale. A massive market could also be opened up for ultra-thin layers of silver nanowires. These are also transparent, and since they are made of metal wires, they conduct an electric current much better than semiconducting CNTs. At the same time, their electrical resistance is so high that the layers heat up quickly, which could make them ideal for coating car windshields, the blades of large wind turbines or airplane wings to keep them free of ice. Even the heating for car seats, which still relies on wires in the upholstery, could, in the future, simply be sprayed on to the material. "Our spraying technique is perfect for any application that requires such materials to be applied in an even layer over large surfaces," claims Abdellah. In principle, this is also possible with ITO, but it is far too expensive for the regular consumer sector.

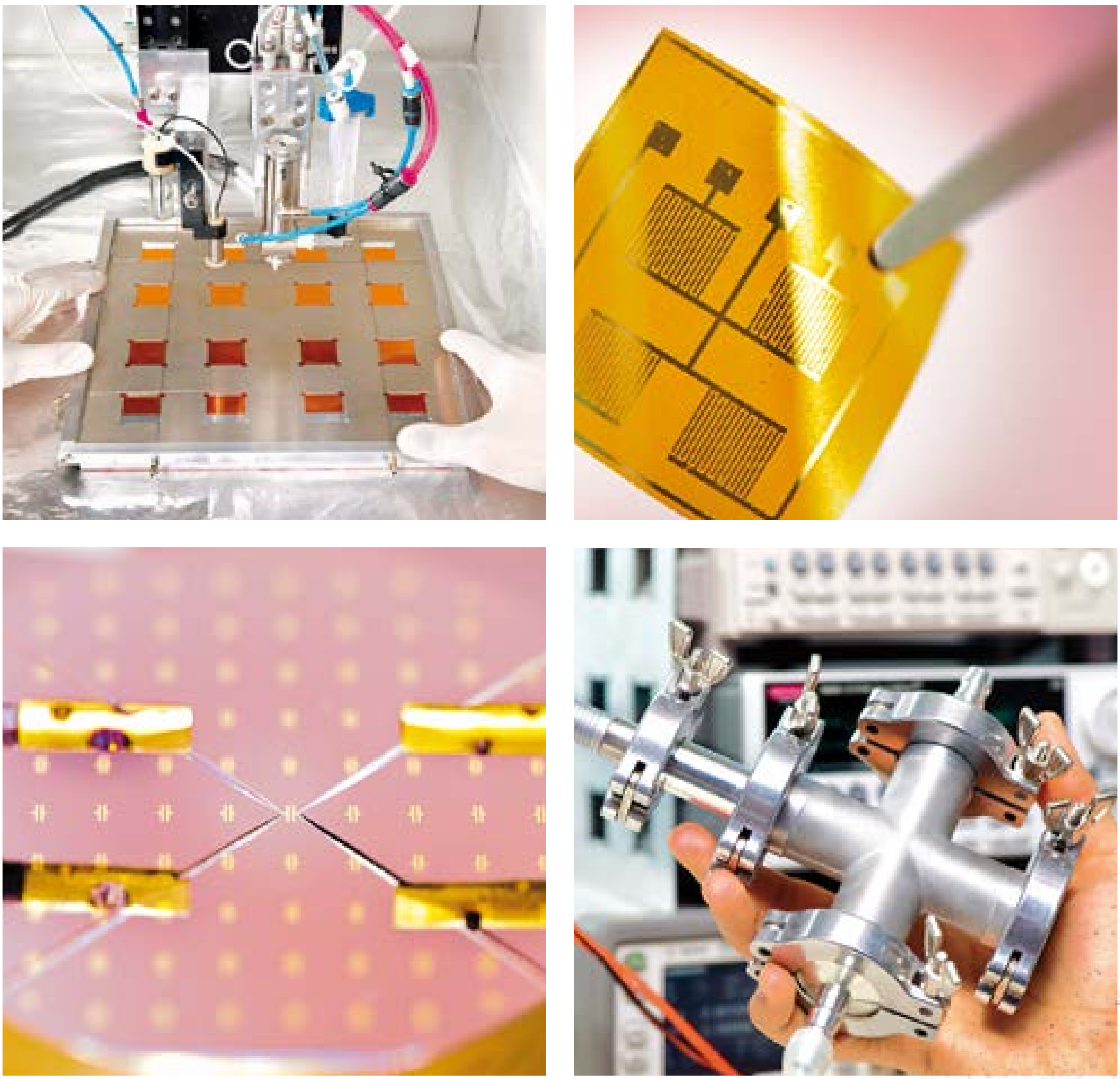
A glimpse into the future

In order to find suitable applications and keep ahead of the competition, the scientists must maintain a large network of contacts and stay up to speed on the latest developments. "We have to remain at the cutting edge of research, which requires us to be smarter and faster than our competitors," says Lugli. "We need to know what everyone else is doing, and do it better than them." Contact with companies is also important, whether on a one-to-one basis or at specialist conferences. Industrial contacts are now being sought to pursue an intriguing vision for the nano-researchers: "We could combine objects created with a 3-D printer with our coating technique," declares Paolo Lugli. "Currently, 3-D technologies are limited in the number of materials that can be printed, but we could make printed objects "smart" if we integrate them with functional conductive layers." The researchers are indeed now attempting to integrate their spray coating method in a 3-D printer, and are examining possible applications. "This is a relatively new field of technology, but I am absolutely convinced that it is going to bloom in the near future," Lugli concludes.

Brigitte Röthlein



The basic principle of the high-tech spray nozzle is not unlike conventional air brushing. But here, everything must be perfect to ensure that extremely thin layers can be applied evenly. The Munich-based researchers have become adept at producing homogeneous inks from the exotic substances, adhering them to the substrate and achieving a perfectly even spray film.



Picture credits: Filser/graphics: ediudsepp

Tried and tested: Coatings are applied to a film in the spray chamber (top left). The template ensures that the correct shape is maintained. The finished part – in this example, a prototype for a flexible gas sensor based on carbon nanotubes (top right) – will first be tested for its electrical properties (bottom left), followed by further testing for its sensing functionality with a variety of gases (bottom right).

Picture credit: Filser

Spraying for science: Prof. Paolo Lugli, Chair of Nanoelectronics at TUM, is working with his colleagues to apply ultra-thin layers of state-of-the-art materials onto a variety of substances. They have discovered that simple methods like spray deposition and inkjet printing – both tried-and-tested industrial processes for inks and paint – are also suited to innovative applications.