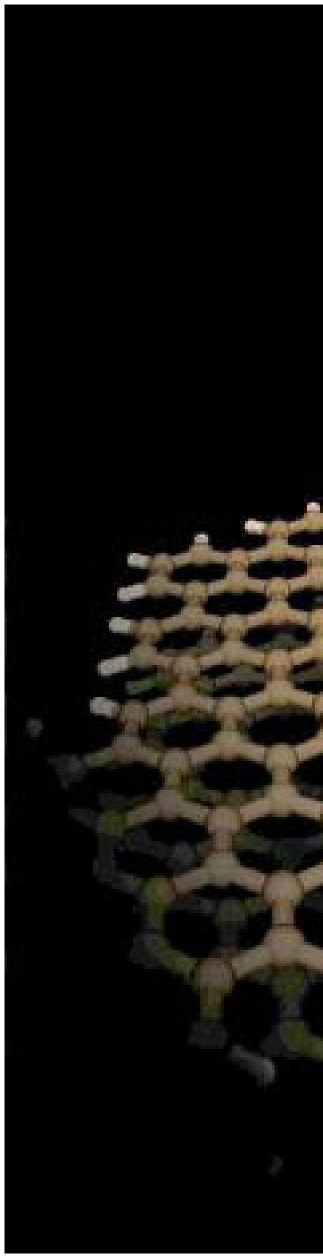
Towards tomorrow's nanoelectronics

To fabricate ever smaller electronic components, new materials are in great demand – for example, ultra-thin layers of carbon known as graphene. As part of an international collaboration, Empa researchers are developing new methods to "grow" these layers in a tailored way on surfaces. To "equip" them with desired properties, the Empa team is also investigating the details of how the structures form – using, among other things, computational modelling.

TEXT: Beatrice Huber / PHOTOS: Empa


Structural model of a graphene ribbon with a zig-zag shape.

Graphene is a very unique material. It consists of a carbon layer only a single atom thick in which the atoms are arranged in hexagons, resembling a honeycomb. Graphene is harder than diamond, extremely tear-resistant and impermeable for gases, and it's also an excellent thermal conductor. When rolled up, this material produces carbon nanotubes; when it's stacked in layers, the result is graphite, which is well known, for instance as pencil lead.

In addition, because of its outstanding electronic properties, graphene is recognised as a possible material to substitute for silicon in semiconductor technology. It's no wonder that graphene and related materials are currently among the hottest research topics. In fact, the Dutch physicist Andre Geim was just awarded the 2010 Nobel Prize in Physics along with the Russo-British physicist Konstantin Novoselov for their groundbreaking work on graphene. Their research team was the first to successfully isolate free-standing graphene layers, something that astounded the scientific community because strictly two-dimensional structures should not actually be stable.

Wanted: a silicon replacement

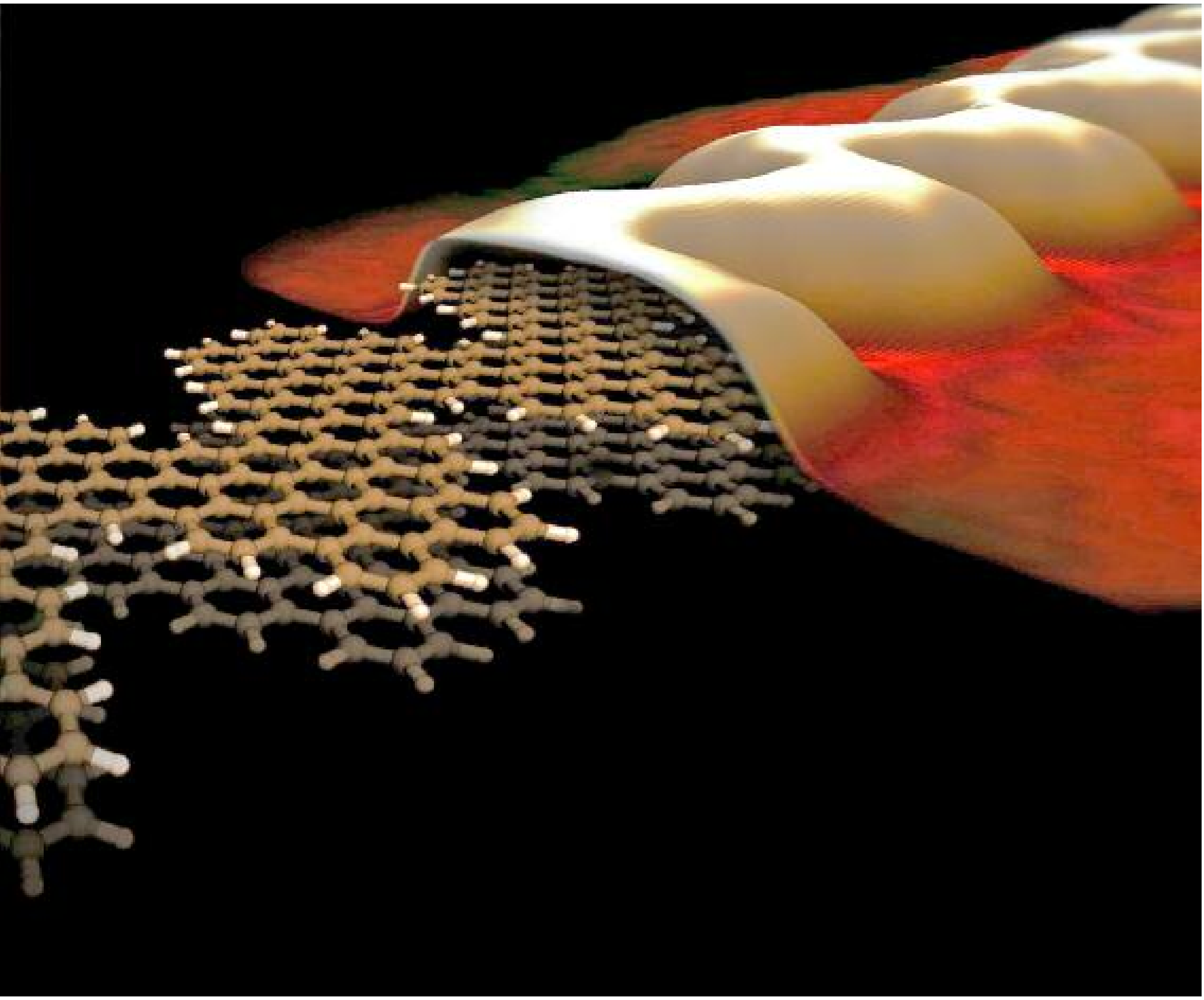
Today, almost nothing happens in semiconductor technology without silicon. One example is the field-effect transistor (FET), the type of transistor most frequently used. Especially for the FET, graphene exhibits properties which could allow a tremendous leap in miniaturisation.

FETs generally have three terminals: the source, gate and drain. The gate controls the transistor by allowing or inhibiting the flow of current from the source to the drain. To do so, the gate either builds up or closes a "channel" between the two other terminals. Graphene now makes it possible to build this channel so it is just a single atomic layer thick, a decisive step towards the further miniaturisation of electronic components and thus towards nanoelectronics. Such thin channels are impossible to produce with silicon, the most common base material in semiconductor technology.

Turning Graphene into a semiconductor

Before graphene and related materials can be used in semiconductor technology, however, several obstacles must be overcome. For one: pure graphene is not a semiconductor. What are known as band gaps, which enable an insulating state, do not exist in graphene. This means that graphene does not allow itself to be "turned off" but instead permanently conducts electricity.

Researchers in Empa's nanotech@surfaces Laboratory are working together with scientists at the Max Planck Institute for Polymer Research in Mainz (Germany) and other institutions on graphene-like materials with band gaps whose size can be set very precisely. One candidate consists of ultra-thin graphene ribbons; another is "porous" graphene, a sheet-like polymer with "holes" of a controlled size and spatial distribution.



Progress towards easy manufacturing

The focus is on methods to produce these graphene-like materials, with their well-defined band gaps, as easily as possible and in ways which are reproducible. “Here we’re employing a ‘bottom-up’ process, specifically molecular self-organisation,” explains Roman Fasel, senior scientist in the nanotech@surfaces Laboratory. “That’s because the conventional methods used until today are not sufficiently precise.” Before components made of these materials can allow custom-engineered optical and electronic properties, the graphene ribbons, for instance, must be extremely narrow, considerably less than ten nanometres wide, and further must have well-defined edges. The “top-down” methods typically used until now cannot achieve these geometries. In those methods, the ribbons are “cut” from graphene layers, or nanotubes are slit open lengthwise and unfurled.

Molecular self-organisation achieves the required precision. In this process, the molecular building blocks join together spontaneously at chemically-defined linking sites and build up a regular structure with the desired electronic properties. The building blocks consist of organic molecules, known as polyphenylenes, which possess halogens (bromine or iodine) at “strategically correct” positions. The geometry of these building blocks and how many halogens are located at which positions then determine what the end product looks like, in other words, whether a ribbon or a sheet-like structure with pores is created.

Ribbons – just a single nanometre wide

Thanks to suitable building blocks, Empa researchers Pascal Ruffieux, Jinming Cai and Marco Bieri together with their colleagues recently manufactured atomically thin graphene ribbons with a width of one nanometre and a length of up to 50 nanometres. “The result is that our graphene ribbons are so narrow that they have electronic band gaps and now exhibit the switching properties of silicon,” says Fasel in discussing the research findings.

But the Empa team didn’t stop there. Depending on which building blocks they used, graphene ribbons develop with various spatial structures: straight, bifurcated or in a zig-zag shape. This work was published last July in the renowned scientific journal *Nature*. With the same methods, it was also possible to successfully manufacture a porous graphene whose pores are only a few atoms in diameter, and whose pattern repeats on a subnanometre scale. This material likewise has the desired band gaps.

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So that the new synthesis methods indeed become a reliable tool with which both graphene ribbons and porous graphene can be manufactured with the desired properties, the reaction pathway must be understood to the last detail. "We want very specific knowledge of the reaction steps," notes Fasel, listing some questions of interest. Which processes are taking place here? Which intermediate products are produced? What forces are involved? What role does the substrate play?

Reaction pathway elucidated with experiments and simulations

In order to answer questions such as these, the researchers combined empirical observations, in particular from a scanning tunnelling microscope, with computer simulations. Findings just published in the scientific journal *Nature Chemistry* now describe the detailed reaction pathway whereby "model building blocks" couple themselves into a planar nanographene. This reaction runs through six steps with five intermediate products, two of which are stabilised sufficiently on the surface so that they can be identified with a scanning tunnelling microscope. And this was exactly what was predicted by the computer simulations.

So far, so good. But if these novel materials are to be useful in electronic circuits, they must be manufactured on semiconductor surfaces. And until now, scientists have fabricated graphene ribbons and porous graphene only on metal substrates. Besides self-assembly directly on a semiconductor, an alternative is to transfer the materials from metal to semiconductor surfaces. "Right now we're working at full speed on both approaches," says Fasel, "and the initial results already look very encouraging." //

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Under ultra-high vacuum conditions, the desired building blocks (in this picture 10,10'-dibromo-9,9'-bianthryl monomers) are applied to a gold surface. In the first reaction step, the building blocks are linked to form polyphenylene chains. In the second step involving high temperatures, hydrogen atoms are removed and the result is a planar, aromatic graphene system – graphene nanoribbons.

2
Straight, bifurcated or in a zig-zag shape: by selecting suitable building blocks, graphene ribbons can be synthesised in the desired shape.

Literature references

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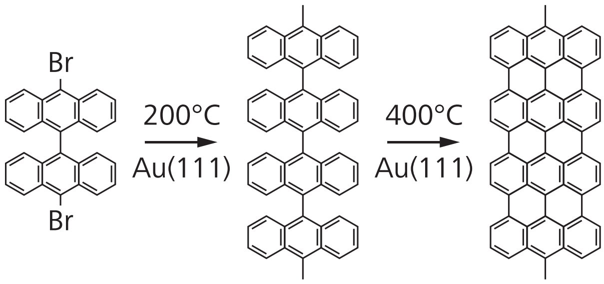

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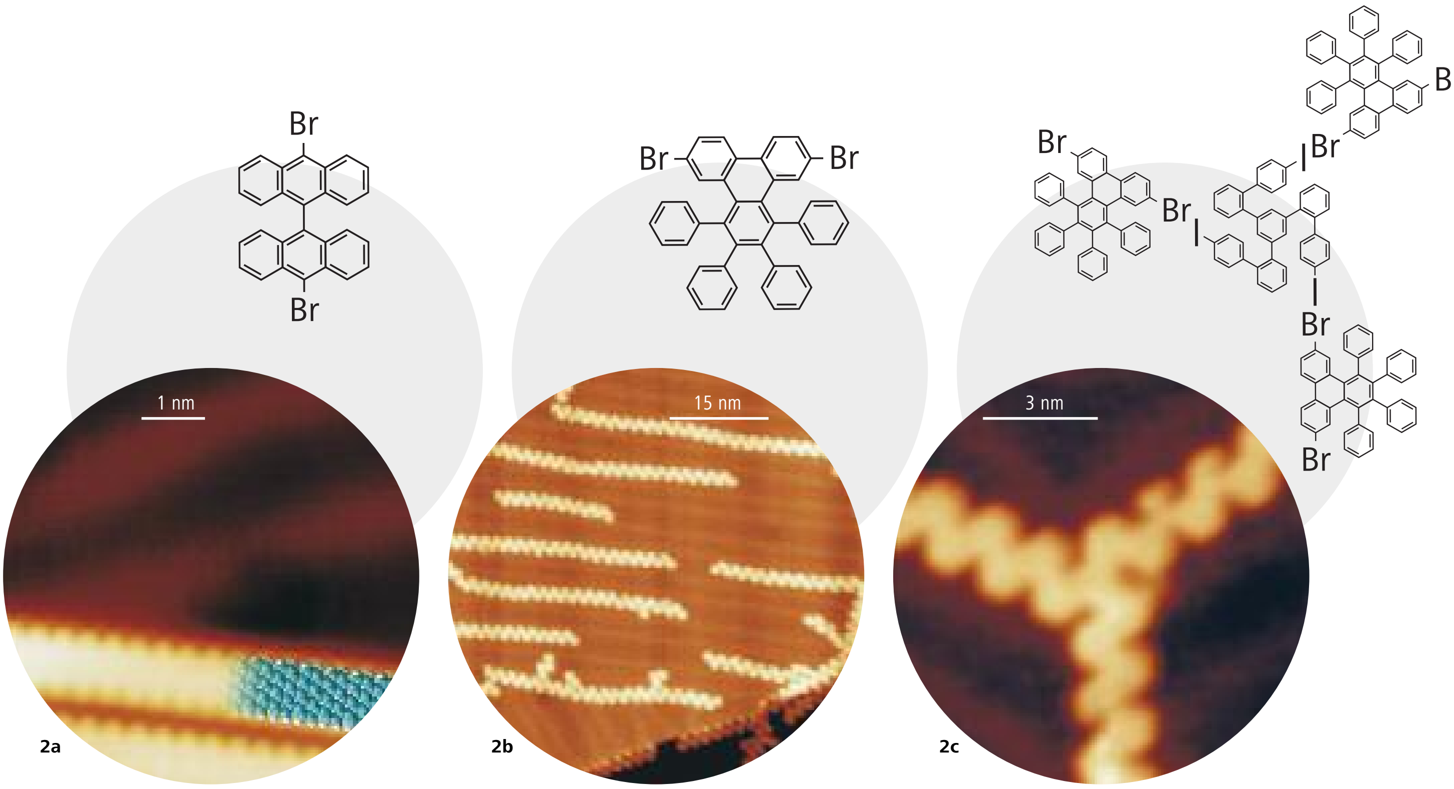

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