

even though only one is stable in the bulk semiconductor. With a series of beautiful images, these groups have shown how a careful choice of growth temperature¹⁰, wire diameter^{10,11} and doping level¹¹ can generate InP nanowires with either structure: wurtzite dominates at lower diameter or growth temperature, whereas zincblende is seen in wider wires or wires doped with zinc. Changes in temperature or doping level during growth therefore create axially modulated wires with segments of each structure.

This is interesting in its own right because wurtzite and zincblende InP have different band structures, suggesting new possibilities for engineering the electronic structure of the nanowire. However, even more remarkable is the structure seen in pure zincblende InP nanowires (Fig. 1d): these nanowires exhibit a particular crystal defect known as a 'twin plane'. Although random twin planes are common, here they occur periodically. In other words, a fault that we previously had no control over could become the basis for a new kind of structure. The spacing between twin planes depends on diameter but is constant in a given wire. Furthermore, the facets which make up the sidewalls of the wire switch orientation at each twin, giving the nanowire the appearance of a stack of octahedra. Periodically twinned superlattices are predicted to give rise to new and potentially useful electronic properties

(including the formation of mini-bands and the opening of gaps). The periodic structure of the faceted surface may also enhance phonon scattering, which is relevant for thermoelectric applications.

How can these results be explained? Nanowires grow by nucleating one layer at a time at the interface between the seed particle and the semiconductor. The choice between wurtzite and zincblende, or between the presence or absence of a twin plane, comes down to the alignment of atoms in the newly forming layer with respect to atoms in the previous layer. The preferred alignment depends on the energies of the various possible configurations of the first few atoms in the newly forming layer. The energy of a given configuration can be influenced by supersaturation, the presence of dopants or the type of sidewall facet created by the new layer, and the preference for one type of sidewall facet over another may depend on the overall geometry of the wire tip. As a zincblende segment grows, the inclination of its sidewall facets forces the interface between wire and particle to become more triangular. Energetic considerations then favour nucleating a twin plane to allow the interface to return to a more hexagonal shape. Thus, we can understand these beautiful structures semi-quantitatively, although the extreme regularity of the spacing between twin planes still requires explanation.

The two teams have shown that in nanowires, we can achieve an unprecedented

control of crystal structure and include structures that are unstable in the bulk. When we grow nanowires, the constraints of thin film epitaxy are removed. Lattice strains are no longer in control; instead, sidewall energy and the geometry of the interface between the particle and the nanowire become important. The choice of particle material and the control of minority species, such as dopants or surfactants, provide new opportunities for material interactions that influence kinetics and thermodynamics, and hence the resulting structure. Given these rich possibilities, what new phenomenon will arise next in nanowires, these fascinating nanoscale materials synthesis laboratories? □

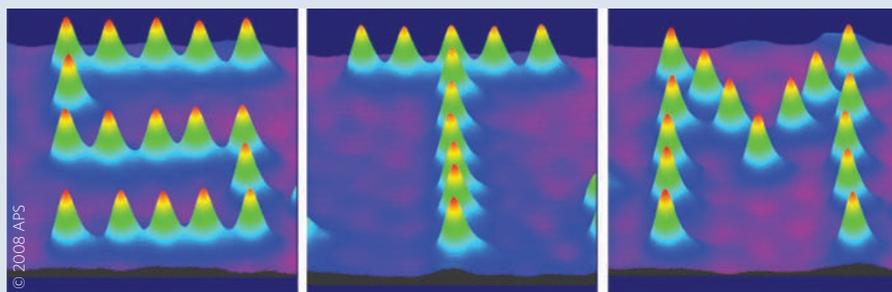
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SURFACE PATTERNING

Electric fieldwork



Scanning probe microscopes are routinely used to pattern surfaces by pushing and pulling single atoms or molecules across the surface with the tip of the microscope. Now, Michiaki Ohara, Yousoo Kim and Maki Kawai at the RIKEN Surface Chemistry Laboratory in Saitama and the University of Tokyo have moved molecules on a surface with a scanning tunnelling microscope (STM), without actually touching them

(*Phys. Rev. B* **78**, 201405; 2008). By using a local electric field produced by the tip, rather than the tip itself, there is less risk of damaging the microscope or breaking up the molecule.

Kim and co-workers placed a negatively charged STM tip just above the centre of a methylthiolate molecule on a copper surface. Electrons tunnelling from the STM tip to the copper surface

excite vibrations in the methylthiolate molecule, causing it to jump randomly in one of three directions defined by the copper lattice.

To achieve some level of control over the jumping direction, the researchers positioned the STM tip just off the molecule centre. In this case, the molecules always jumped directly away from the STM tip — a process the team called 'repulsive-hopping'. The molecules could also be made to jump towards the tip, by reversing the electric field.

The Japanese team demonstrated the potential of their approach by spelling out the letters 'S', 'T' and 'M' with methylthiolate molecules on the copper surface. Each of the images shown above is 6 nm across.

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