MATERIALS SCIENCE

Screen printing of 2D semiconductors

Atomically thin semiconductors have been made by transferring the oxide 'skin' of a liquid metal to substrates. This opens the way to the low-cost mass production of 2D semiconductors at the sizes needed for electronics applications.

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The integrated circuits used in today's electronic devices rely on the patterning of materials by photolithography[1], a modern adaptation of the 221-year-old lithography printing technique[2]. The success of photolithography in creating complex circuits over hundreds of square centimetres has motivated the development of other techniques for patterning materials on the micro- and nanoscale, many of which are also inspired by older methods. These include direct stamping, 'dip-pen' lithography, nanoimprint lithography and ink-jet patterning[3]. Writing in *Nature Communications*, Carey *et al.*[4] describe a technique for generating patterns of atomically thin semiconductors that can be seen as a new form of screen printing — a technique many centuries older than lithography[5].

Two-dimensional semiconductors are promising materials for next-generation electronics — in particular, large-area, flexible electronics and optoelectronics — because of their good charge-carrier mobility and outstanding mechanical properties. However, new strategies for the deposition and patterning of these materials[6] are required for the mass production of low-cost flexible electronics. So far, several methods have been demonstrated for the isolation and synthesis of 2D materials. The simplest one is the mechanical removal of sheets of atoms from layered crystals using adhesive tape[7]. This allows highly crystalline flakes to be made, but with low yield. Moreover, the flakes are irregularly shaped and are just a few tens of micrometres long, which is not suitable for large-scale applications.

Methods for growing larger samples of 2D materials have therefore been investigated. Great progress has been made using techniques called chemical vapour deposition (CVD)[8] and metal–organic chemical vapour deposition (MOCVD)[9], in which one or more volatile precursors react or decompose on the surface of a substrate to deposit the desired material. These techniques have enabled the growth of materials on hard substrates such as silicon dioxide and sapphire, over areas of up to tens of square centimetres. However, they require relatively high temperatures (greater than 550 °C), which precludes direct growth on flexible polymer substrates. Moreover, the long growth times required (about 26 hours for centimetre-scale MOCVD growth) are a challenge for mass production.

The most commonly studied 2D semiconductors have been transition-metal dichalcogenides such as molybdenum disulfide, but other materials, for example gallium(II) sulfide, are now attracting increased attention, because they hold promise for applications that include flexible and transparent transistors and gas sensors[10]. Gallium(II) sulfide belongs to a class of material that has the general formula MX, where M is a metal from group III of the periodic table and X is a chalcogenide such as sulfur, selenium or tellurium. These materials form sheets in which atoms are packed in hexagonal lattices, similar to the carbon atoms in graphene, and stacked so that two layers of M atoms are sandwiched between two layers of X atoms (an X–M–M–X pattern). Like graphene and other layered materials, the interlayer bonding is relatively weak, so that individual monolayers (in this case, consisting of X–M–M–X units) can be isolated.

Carey *et al.* realized that MX materials based on the group-III metal gallium provide an opportunity to develop a new method for 2D-semiconductor synthesis and patterning. Gallium has a low melting temperature (29.7 °C) and forms an atomically thin oxide layer under atmospheric conditions. Moreover, gallium oxide adheres well to other oxides that are commonly used as substrates for electronics (such as silica; SiO_2), whereas liquid gallium does not.

The authors therefore found that, by melting gallium on silica substrates and scraping away the metal, they could transfer an atomically thin layer of gallium oxide onto the substrates (Fig. 1). What's more, by using a substrate that was treated so that some areas would not adhere to the gallium oxide, they produced patterns of gallium oxide on silica. This strategy is akin to the process used to apply ink to paper or fabric in screen printing, and provides quick patterning and uniform transfer of the atomically thin oxide to the substrate — without using expensive or high-temperature processes.

A second process is essential for transforming the gallium oxide into gallium sulfide. Direct sulfurization of the chemically inert gallium oxide layer is not a viable option because of the high temperature required (greater than 900 °C)[11]. Carey *et al.* therefore used a two-step process in which the oxide is first transformed into gallium(III) chloride by exposing it to hydrochloric acid vapour at 45 °C. They then exposed the chloride to sulfur gas at 300 °C, transforming it into gallium(II) sulfide. This temperature is low enough to be compatible with standard industrial methods for semiconductor processing, and with the use of some flexible substrates. The authors' overall

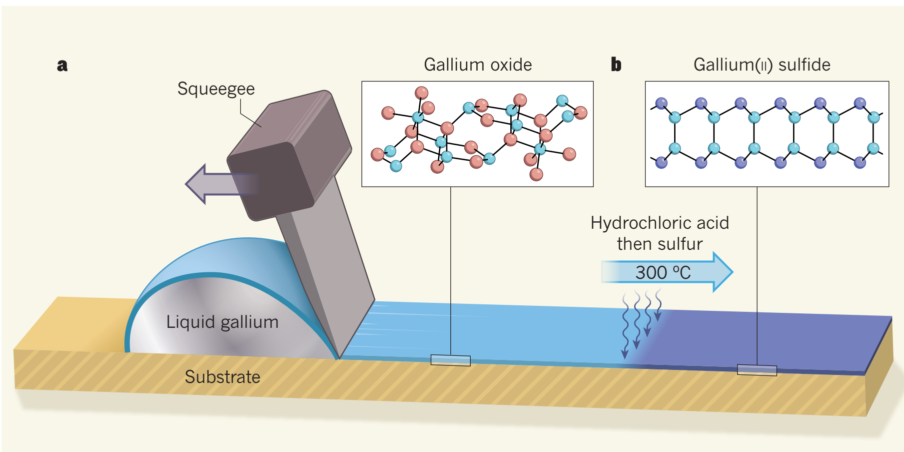

Figure 1 | A method for making atomically thin layers of gallium(II) sulfide. a, Liquid gallium forms an atomically thin layer of gallium oxide under atmospheric conditions. Carey *et al.*[4] report that when liquid gallium is scraped across the surface of a silica substrate using a 'squeegee', the liquid metal is pushed away, but the oxide layer sticks to the surface. **b**, The authors treated the oxide layer with hydrochloric acid vapour, and then with sulfur vapour at 300 °C, to form an atomically thin layer of the semiconductor gallium sulfide. The method opens the way to the production of 2D patterns of gallium sulfide, which are needed for electronics applications. In the insets, gallium is shown in light blue, oxygen in red and sulfur in dark blue.

strategy — oxide screen printing followed by two-step sulfurization — thus enables the synthesis of uniform layers of 2D semiconductors at relatively low temperatures, and could be scaled up for mass production using low-cost processes such as roll-to-roll printing[12].

Several issues must be addressed to improve the quality of the films obtained, for use in high-performance devices. Carey *et al.* report that the electronic mobility of their films is better than that previously reported[13] for ultrathin gallium(II) sulfide, but still inferior to that obtained for films of transition-metal dichalcogenides prepared using CVD[8] and MOCVD[9]. The films are continuous over areas of only about 10 μm^2, although the authors demonstrate that many micrometre-sized devices can be printed across areas of several square centimetres.

Further research will be needed to controllably introduce 'dopant' elements into the deposited material, to allow the production of n- or p-type gallium(II) sulfides that conduct using negative or positive charge carriers, respectively. Ideally, these would be serially deposited in the same way that different inks are used in colour screen printing, to create complex devices such as transistors and diodes. Finally, it remains to be seen whether this technique can be expanded to other members of the MX family, such as indium(II) sulfide and gallium(II) selenide. Nevertheless, Carey and colleagues' work offers great prospects for large-scale, low-cost printing. These advances potentially position 2D semiconductors derived from liquid metals as the materials of choice for printed, bendable optoelectronic devices. ■

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BIOCONTROL

Crown-of-thorns no more

The starfish *Acanthaster planci* destroys coral reefs. Whole- genome sequences provide clues to the proteins that mediate *A. planci* outbreaks — information that might be used to help protect coral. SEE LETTER P.231

MÓNICA MEDINA

Coral reefs face many threats, not least of which is the risk of recurrent outbreaks of *Acanthaster planci*, the crown-of-thorns starfish (COTS). A ferocious predator of reef-building corals, aggregations of COTS can denude kilometres of reef during outbreaks[1] (Fig. 1). Contending hypotheses for the cause of COTS outbreaks range from increases in nutrients and pollutants in the water column to warming sea surface temperatures[2]. On page 231, Hall *et al.*[3] report whole-genome sequences for *A. planci*, and perform analyses that provide much-needed momentum in the quest to curtail outbreaks of this starfish.

The authors sequenced two COTS individuals from distant regions of the Pacific Ocean — one from the Great Barrier Reef in Australia, and one from off the coast of Okinawa, Japan. Comparison of these genomes revealed high similarity in gene content and sequence identity (about 99%), in line with what is typically observed in marine animals that, like COTS, spawn by releasing eggs and sperm into the water, and have large population sizes and high dispersal capabilities. Coalescent analysis (in which computational models reconstruct the demographic history of populations using genomic information) suggested that the two COTS populations underwent similar changes in size over geological timescales, with an initial decline and subsequent recovery in the late Pleistocene, about 50,000 years ago.

Genetic analyses of COTS samples taken from many of the disparate marine regions in which the starfish are found have previously provided evidence[4] that *A. planci* is actually a species complex, consisting of four distinct clades that arose from an initial lineage in the Indian Ocean — Northern and Southern Indian Ocean clades, a Red Sea clade and a Pacific Ocean clade. Hall and colleagues' genomes afford a high-quality reference for future population-genomics analyses within and across the four clades. Such analyses could enable the identification not only of population-specific genetic variants, but also of local sequence adaptations to a particular environment[5].

The researchers compared their COTS genomes with those of other sequenced deuterostomes (the group of animals that includes vertebrates, echinoderms such as starfish and sea urchins, and hemichordates such as acorn worms), with the aim of identifying COTS-specific genes that could be targeted for biocontrol. This revealed some evolutionary conservation between the chromosomes of COTS, sea urchins and hemichordates. It also revealed that only a few gene families have more members in COTS than in related taxa, narrowing the authors' search for lineage-specific genomic innovations. Analysis of the complete collections of gene transcripts (the transcriptome) in various COTS tissues revealed that these expansions are in gene families that encode secreted proteins and receptor proteins expressed in external organs such as the spines, body wall and mouth region, indicating that they might be involved in communication between individuals.

Chemical communication is essential for species that live on the ocean floor to find mates and escape predation. COTS respond to chemical stimuli from other individuals by aggregating (known as positive chemotaxis) before mass spawning events. Hall *et al.* next investigated the molecules that might mediate these responses using a Y-maze choice experiment, in which the starfish moved down a channel then took either a left or right channel on reaching a junction.

The authors exposed starfish to a channel that contained proteins released from aggregating COTS and to a control clean water channel. They then performed a similar experiment using proteins from a predator, the giant triton snail *Charonia tritonis*. The aggregate exposure led to positive chemotaxis, whereas predator exposure resulted in negative chemotaxis, with COTS moving away from the signal. The researchers analysed water samples to identify all of the proteins (the proteome) secreted by COTS in response to each stimulus. This uncovered approximately 400 proteins that were released into the water by the starfish during aggregation, predator evasion