devices. Furthermore, separation and recombination of photoinduced electron–hole pairs at a heterojunction interface are primary mechanisms governing the operation of solar cells, photodetectors and light-emitting devices. Both Gong and collaborators and Duan and colleagues managed to electrically address the lateral heterojunctions and perform transport measurements to investigate their electrical behaviour. Even though the contacted structures are not predefined in shape and thus are far from optimized devices, rectifying behaviour across the junctions was clearly observed, showing a concrete proof of principle. Both groups also showed clear evidence of the photoresponse of the heterojunctions in their transport measurements. Similarly, charge recombination at the lateral heterojunctions has been characterized in the three studies by means of photoluminescence imaging, which revealed an enhanced emission response at the interline between the materials in all cases. Mastering the in-plane growth of different TMDs down to the single-atom level could enable the synthesis of laterally quantum-confined systems, with promise of exciting physics. Also, this could open up opportunities for a wide range of devices, including complementary logic circuits, high-frequency devices and photodetectors.

Whereas the lateral junctions show scope for miniaturization, the development of larger scale vertical heterojunctions will prove crucial for commercial applications in light emission and light harvesting. Large-scale photodiodes using vapour-phase-grown MoS_2 transferred to silicon wafers have been realized already[12]. They have shown impressive performance and have also revealed that using vapour-phase-grown materials allows tuning of the optical response of the device. However, the *in situ* growth of a bilayer heterojunction could largely improve on this, in particular by engineering pristine interfaces that are not achievable by transfer techniques. Further optimization of the CVD process will lead to better control over the grown structures and over the interface quality. Future work will extend these approaches towards other material sets with arresting discoveries yet to come. ❐

Georg S. Duesberg is at the Centre for Adaptive Nanostructures and Nanodevices (CRANN) and the Advanced Materials BioEngineering Research Centre (AMBER), School of Chemistry, Trinity College Dublin, Dublin 2, Ireland.
e-mail: duesberg@tcd.ie

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2D CRYSTAL SEMICONDUCTORS

Intimate contacts

High electrical contact resistance had stalled the promised performance of two-dimensional layered devices. Low-resistance metal–semiconductor contacts are now obtained by interfacing semiconducting MoS_2 layers with the metallic phase of this material.

Debdeep Jena, Kaustav Banerjee and Grace Huili Xing

Transistors and lasers made of semiconductor materials power the information age by providing the building blocks for electronic switching, amplification and photonic communication. The electronic and photonic properties of the semiconductor play a primary role in determining the performance of such devices, yet comparable importance resides in the way this material interfaces with the external metallic circuits. A high electrical resistance due to a high energy barrier — the Schottky barrier — encountered by the charge carriers moving through the metal–semiconductor contacts saps the energy efficiency, and significantly degrades the performance of the device.

Semiconductor researchers are excited about the potential of transition metal dichalcogenide (TMD) layered semiconductors. For device applications, the excitement is fuelled by the dream of improving device performance by using a semiconductor channel that is potentially one monolayer thick[1]. The first generation of field-effect transistors made from MoS_2 and related TMDs have shown promise, but trail the silicon and III–V semiconductor analogues significantly in performance. A high contact resistance is the root cause. Writing in *Nature Materials*, Rajesh Kappera and colleagues now report an unconventional method to address this problem head-on[2], based on the local conversion of MoS_2 semiconducting layers into a metal that lowers the barrier to the charges flowing in the external circuits.

The traditional method to lower the contact resistance between a metal and a semiconductor relies on an intermediate layer, usually a heavily doped semiconductor that helps charge carriers from the metal to be injected in the conduction and valence bands of the semiconductor. The metal is chosen based on its workfunction, so that it creates a low Schottky barrier height with the semiconductor contact region, whereas heavy doping reduces the thickness of the barrier, enabling a significant fraction of electrons to quantum mechanically tunnel through it. However, chemical doping has proven challenging with TMD semiconductors. In their work, Kappera *et al.* exploit the fact that MoS_2 exists in two crystalline phases: the 2H and 1T types, which differ in their stacking geometry. The 1T phase is obtained by twisting one set of the 2H Mo–S tetrahedron by a 60° rotation. The stable 2H structural phase has a semiconducting behaviour and is desired as the channel of the transistor. The 1T phase is structurally metastable, but can be stabilized if electrons are pumped into it — it then becomes metallic because of a half-filled *d*-orbital band. This electronic stabilization of the metallic 1T phase can be achieved by converting the 2H phase by various routes, for example by irradiation with an electron beam[3]. Kappera and

colleagues use a chemical technique, treating the MoS_2 with an organometallic solution containing *n*-butyl lithium. Lithium donates electrons to the 2H MoS_2 converting it into the 1T metallic phase. The chemical process achieves the phase transition selectively: covered areas are left semiconducting, and exposed areas become metallic, as confirmed by extensive chemical, structural and optical analytical characterization. When the solution is washed away, the 1T region is likely to attract immobile positive charges and remain stable. Such a semiconductor-to-metal phase-transition process can be amenable in a device fabrication environment.

The team then used this process to make batches of transistors — the test structures have 1T metallic MoS_2 source–drain contact areas interfacing gold pads, and the control structures have direct gold–2H semiconductor MoS_2 contacts. In the test devices, the contact resistance was found to drop from ~1–10 kΩ μm to ~0.2–0.3 kΩ μm. As a result, the performance of the 1T contact transistors was significantly superior across the board of metrics: the drive current, the sharpness of switching and the gain all improved. The researchers also find that the 1T contact transistors have a much higher reproducibility and yield compared with their 2H contact counterparts. The transistor characteristics are also less sensitive to the workfunction of the metals, suggesting that the contacts' performance now mainly depends on the 1T/2H interface. Other TMD semiconductors have similar metallic counterparts, implying the same principle potentially applies to them.

The phase-engineering approach to making low-resistance ohmic contacts to TMD semiconductor materials is thus an exciting advance that addresses a critical problem holding back potential applications. As with any new study, a list of unknowns remains to be worked out. By itself, the 1T metallic phase of MoS_2 is negatively charged — meaning the identity of the neutralizing positive charges that are presumably immobile remains to be determined and controlled. The nature of the 1T–2H metal–semiconductor junction, the band alignments, and a potential way to contact the valence band for hole conduction need to be developed. The barrier between the metal and 1T phase due to weak van der Waals bonding needs to be investigated. The lateral diffusion of the organometallic lithium solution under the covered areas can convert part of the desired 2H MoS_2 channel into the 1T phase, whereas the chemical conversion of the exposed regions is not perfect; alternative ways to seal the channel during the chemical

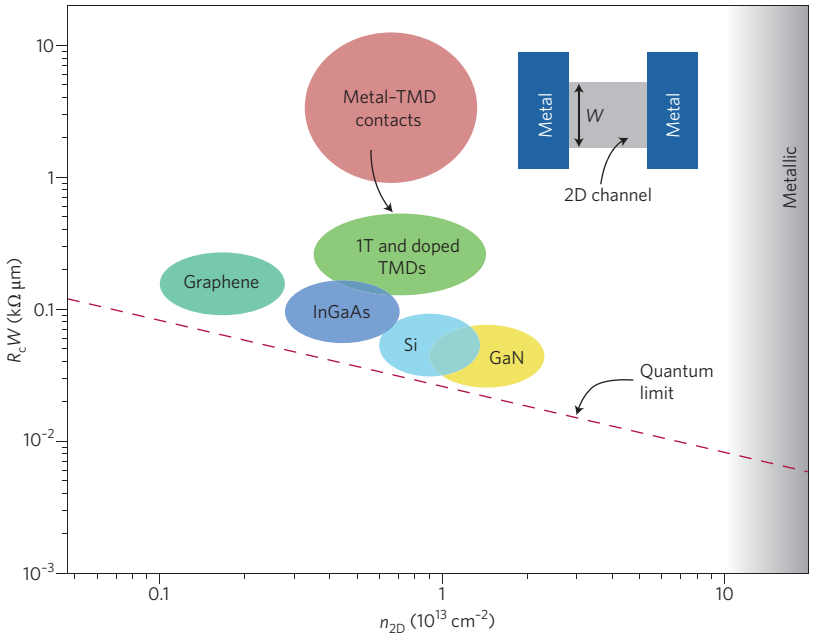

Figure 1 | Contact resistances for various semiconductor materials against the quantum limits for crystalline materials. Using a 1T metallic phase to interface MoS_2 with metals shifts the performance of TMD-based transistors closer to the quantum limit predicted by Landauer and Sharvin. The inset shows a typical transistor configuration.

treatment and achieve complete phase transformation in the contact areas need to be investigated. And as the researchers state, the stability of the 1T contacts under high-performance operation — for example when large currents are driven through the transistor — remains to be elucidated.

But how low a contact resistance can one obtain? This problem in various forms has been studied for more than a century. James Clerk Maxwell calculated[4] the classical 'contact' resistance between two regions of conductivity σ separated by an insulator and connected by a conducting circular constriction of diameter D to be $R_c \sim 1/(\sigma D)$. In the 1950s and 1960s, Landauer[5] and Sharvin[6] gave the problem a quantum facelift. Their work predicted a minimum contact resistance value for $R_c \sim h/(2e^2M)$, where h is Planck's constant, e is the electron charge and M is the number of electron modes whose wavelength fit the narrow conductor. In other words, even for a perfect conducting channel with no scattering, only those electron modes that fit are allowed access into the channel, the rest are reflected. As the sheet density of electrons $n_{2D} = k_F^2/2\pi$ in a two-dimensional (2D) channel increases, the wavelength $\lambda = 2\pi/k_F$ of the energetic electrons riding the Fermi surface shortens, and more modes $M \sim k_F W$ fit, where W is the width of the channel and k_F is the Fermi wavevector. The minimum contact resistance is then $R_cW \sim h/2e^2k_F \sim 0.026/\sqrt{n_{2D}}$ kΩ μm, which depends strongly on the electron sheet density (in units of 10^{13} cm^{-2}) in the semiconductor channel, and weakly on some aspects of the bandstructure[7]. This is the quantum limit of the contact resistance for crystalline semiconductors, shown by the dashed line in Fig. 1.

This limit has been experimentally verified in atomic break-junctions and in split-gate quantum point contacts, in which a quantized conductance was observed[8]. The highest-performance semiconductor transistors are also grazing this lower limit[9], as shown in Fig. 1. The latest achievements for TMDs represent a major leap, yet there is still room for improvement. Recently, a joint academic and industry research team has reported a method to chemically dope MoS_2 and have achieved low-resistance contacts and high-performance transistors[10]. Their technique is similar to the traditional method used for semiconductors, and the contact resistance values are similar to the 1T contacts discussed here. Both these old and new approaches mark important steps towards harnessing the innate potential of 2D crystal semiconductors. More importantly, metal–semiconductor junctions can enable a host of unanticipated physical phenomena exploiting the *d*-orbital pedigree of conduction electrons in TMDs. ❐

Depdeep Jena and Grace Huili Xing are in the Department of Electrical Engineering, University of Notre Dame, Indiana 46556, USA, and in

the Department of Electrical and Computer Engineering, and Department of Materials Science & Engineering, Cornell University, New York 14853, USA. Kaustav Banerjee is in the Department of Electrical and Computer Engineering, University of California, Santa Barbara, California 93106, USA.
e-mail: djena@nd.edu

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BIOMINERALIZATION

Crystals competing for space

Analysis of the growth patterns of calcitic prisms within the shell of the fan mollusc *Pinna nobilis* shows that growth can be predicted using grain theory and that the organic casings of the prisms set the thermodynamic boundaries.

Nico A. J. M. Sommerdijk and Maggie Cusack

Biominerals, such as bone, teeth and shells, are organic–inorganic composite materials with often amazingly complex shapes and structures. Biology uses a variety of minerals to form these structures — most commonly, calcium carbonate ($CaCO_3$) and calcium phosphate, which are used by marine invertebrates and vertebrates, respectively, as well as iron oxides and silica[1]. Growth of biominerals is thought to be controlled by their interaction with a complex organic macromolecular matrix that consists of a specialized dynamic assembly of (glyco)proteins and carbohydrate polymers. As a consequence of these interactions, a high level of control is achieved over the composition, structure, size and morphology of the resulting material[2]. Moreover, through these interactions the structure and properties of the biological hybrids are precisely tuned towards their specific functions: for example, navigation, mechanical support, photonics and protection against predation, often producing physical structures that surpass those of synthetic analogues. However, the extent to which the growth of biominerals is controlled by their interaction with these organic matrices, and whether there is also control through classical thermodynamic parameters, remains unclear.

Writing in *Nature Materials*, Zlotnikov and colleagues now shed light on the shape evolution of calcite prisms in a mollusc, and show that the prismatic structure and morphology can be predicted by classical thermodynamic theories[3]. Using synchrotron-based microtomography, they analyse the mesostructure of the prisms forming the calcitic outer layer of the giant Mediterranean fan mollusc *Pinna nobilis* and conclude that only a minimal amount of biological control is used to create the well-organized prismatic crystals. Indeed, other than setting the boundary conditions of the thermodynamics involved in the process, the findings of Zlotnikov and colleagues suggest that the biological organism has little involvement in the formation of the finer structural detail of the outer layer of its shell.

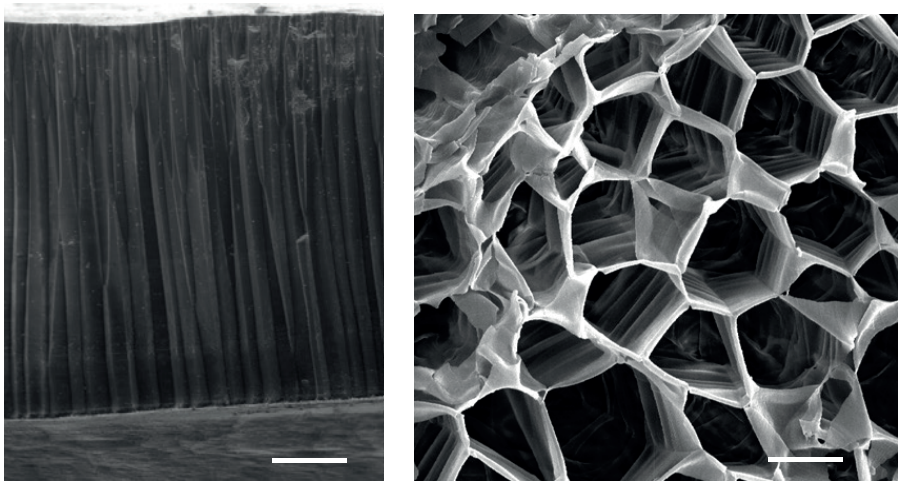

Figure 1 | Secondary electron images of the calcite prisms and organic casings of the shell of the fan mollusc, *Atrina vexillum*. **a**, Fracture section of the shell of *A. vexillum* showing the oriented calcite crystals in the prismatic layer of the shell. Scale bar, 250 μm. **b**, The organic casings in which the prisms grow. The prisms were dissolved by incubation in acetic acid (1 M) for 24 h. Scale bar, 50 μm. Images courtesy of Peter Chung (**a**,**b**) and Maggie Cusack (**b**), University of Glasgow.

Biomineralization has intrigued scientists for many decades and serves as a constant source of inspiration for the development of new materials with highly controllable and specialized properties[4]. Also, because biological materials are normally synthesized in aqueous media and at ambient temperatures — conditions that are prerequisites for the synthesis of green materials — a richer understanding of the biomineralization process may open new sustainable pathways to materials with advanced functional and structural properties. Moreover, the findings reported by Zlotnikov and colleagues point towards the simpler nature of the factors that control this particular biomineralization process, and if similar strategies could be exploited by synthetic chemists the accessibility of green synthesis routes could be greatly improved.

As a result of their abundance in nature, biological materials composed of $CaCO_3$, for example mollusc shells, are the