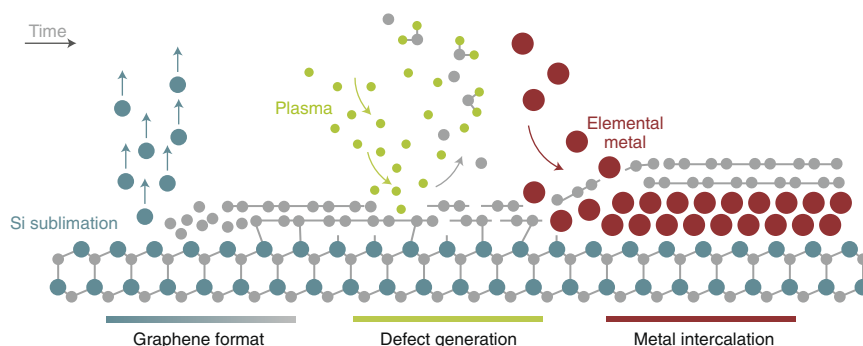2D METALS

Flat and safe under the graphene sheet

Large-scale atomically thin metals can be stabilized through confinement epitaxy at graphene/SiC interface, which exhibit a gradient bonding type and are air stable, providing a compelling platform for quantum and optoelectronic technologies.

Claire Berger and Walt A. de Heer

As this year marks the 40th anniversary of the discovery of the quantum Hall effect (QHE)[1], we are reminded that matter in low dimensions may behave in strange ways. Zero resistance and quantized resistance plateaus in the QHE regime, as well as the persistence or appearance of superconductivity in atomically thin films (such as monolayer Pb, NbSe₂, Tin or bilayer graphene) are just a few examples. At the time of the QHE discovery, tricks were applied to confine electrons electrostatically at the interface between two materials. Today, dimensionality effects can be studied in materials that are as two-dimensional (2D) as they can get: that is, one-atom thick sheets. These 2D materials can be prepared at the interfaces of two crystals, or by deposition on the surface of a substrate, or from naturally layered materials like graphite where in-plane chemical bonds are much stronger than the out-of-plane bonds, allowing easy separation of atomically flat layers[2]. In contrast to layered materials, freestanding ultrathin metal films are unstable: they will spontaneously crumple up and require a substrate to stabilize them. In addition, they are in general extremely sensitive to air and can only be studied using in situ ultrahigh vacuum methods. Now published in *Nature Materials*, Natalie Briggs and co-workers[3] have found a way to easily produce 2D crystalline metals (notably non-noble metals) that can be studied in ambient conditions.

The atomically thin metal layer is sandwiched between a substrate and an over-layer, which provides protection from environmental degradation. But rather than growing a metal film on a substrate and then covering it with a protective coating, here the metal atoms were made to spontaneously squeeze themselves under an epitaxial graphene (epigraphene) layer — a graphene that was first grown on a single crystal silicon carbide (SiC) substrate[4,5]. Epigraphene is known to cover continuously and seamlessly the entire SiC wafer[5]. To promote metal atoms intercalation, the graphene layer was first exposed to

Fig. 1 | 2D metal fabrication. Schematic showing the process from graphene growth via silicon sublimation, to plasma treatment to generate defects, and diffusion of metal atoms through defects (intercalation), realizing an all-epitaxial epigraphene/metal/SiC structure.

oxygen plasma to introduce holes, through which the metal atoms could pass, as shown in Fig. 1. These defects obviously compromise the very protection that epigraphene was to provide. But the high density of defects in graphene apparently 'healed' during the intercalation process at elevated temperatures (~700 °C). Using this technique encapsulated ultrathin films of one to three atomic layers of Ga, In and Sn were produced[3], realizing what the authors called 'half van der Waals metals' where the atoms are bonded covalently to the bottom SiC surface, thereby stabilizing the 2D layer, and at the same time are weakly bonded to the top graphene layer protecting them from the environment. By virtue of the atomic alignment between the crystal lattice of the SiC and that of 2D metals (hetero-epitaxy), the atomic structure of the SiC/metal/graphene heterostructure stack is the same everywhere, which can be reproducibly scaled to the SiC substrate wafer size (commercially available up to 15 cm in diameter).

These 2D metal films are fully crystallized, but even more interestingly, their atomic structure — having a half-covalent (with SiC)- and half van der Waals (with graphene)-bonded characteristic — is distinct from their natural three-dimensional counterpart, giving rise to intriguing properties. For example, a

zero-resistance critical superconducting temperature of 3.2 K for a three-layer Ga film was measured, which is three times that of bulk Ga (1.08 K), and half that of metastable β-Ga (~6 K), but with much higher critical fields. Remarkably, the measurement was performed after the heterostructure had been exposed to air, demonstrating the environmental protection provided by the epigraphene sheet.

Ga, In and Sn are not the only elements that can slip through the graphene sheet to reach the SiC interface. The ease with which foreign atoms intercalate at the SiC/epigraphene layer interface has been known and various degrees of intercalation and stability have been demonstrated with Al, Au, Bi, Cu, F, Fe, FeCl₃, GaN, Ge, H, H₂O, Li, Mn, N, Na, O, Pb, Pt, Pt, Si, Yb and so on[5]. Stabilizing and protecting 2D thin films by intercalation (or 'confinement heteroepitaxy'[3] in the present case) can in principle be widely applied to provide a platform for mediating compelling structural and physical properties. It will be very informative to study other metal heteroepitaxial monolayers. For instance, it was recently shown[6] that continuous gold films fabricated at the epigraphene/SiC interface have unexpected semiconducting properties. Extension of this method to heavy metal Sn can help to investigate exotic pairing mechanisms in 2D

superconductors[7]. In turn, intercalated layers do modify the properties of epigraphene. Separated from the substrate by hydrogen intercalation, the epigraphene layer that was previously in direct contact with SiC (buffer layer) turns from semiconducting to conducting[8]; the epigraphene layer above the buffer layer changes from heavily negatively doped to charge neutral with Sn intercalation[9], or to *p*-doped, controlled by the H intercalation[10].

Atom intercalation opens possibilities even beyond the stabilization of new 2D structures and the study of unknown phenomena at this scale. Epigraphene, this single- or multilayer graphene that forms epitaxially on SiC crystals when they are heated[11] has been developed as a platform for 2D nanoelectronics since 2001[4,5], taking advantage of the perfectly defined interfaces resulting from the SiC/graphene heteroepitaxy, and the transferless

wafer-size scalability provided by the industrial grade single-crystal substrate. Having all-epitaxial 2D heterostructures that can be grown controllably and that can be studied in ambient condition is a formidable playground. One can only imagine the possibilities opened by combining epigraphene properties (room-temperature ballistic conductance, long spin diffusion, sturdy QHE plateaus and so on) with that of magnetic or superconducting 2D metals or other topological materials for investigating topological phenomena, as well as developing spintronics or advanced optoelectronics.   ❐

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ORGANIC ELECTROCHEMICAL TRANSISTORS

Lowering the threshold for bioelectronics

A high-speed, high-gain enhancement-mode ion-gated transistor shows promise for low-power chronically implanted bioelectronic systems.

Scott Keene and Yoeri van de Burgt

Bioelectronic applications aim to link the biological environment with conventional electronic systems. But due to the vastly different nature of both worlds (hard versus soft, electrons/holes versus ions, dielectrics versus liquids), finding optimal materials has proven difficult and has been the focus of the field of bioelectronics for many years. Recently, organic electrochemical transistors — or ion-gated transistors — based on soft and biocompatible materials have been developed to bridge this gap. These devices convert ionic currents from biological media to electronic signals and at the same time reduce the mechanical mismatch with biological tissues. There have been significant demonstrations of IGTs for biosensing and electrophysiological recordings[1], yet they are still limited by their relatively slow speeds (about 1–10 kHz) and high power consumption. Now, writing in *Nature Materials*, Claudia Cea, George Spyropoulos and colleagues have found a straightforward way to modify an ion-gated transitor material to connect electronic

devices with biological environments in a fast, stable and low-power manner[2].

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) has been the basis for a wide variety of applications and is generally considered the most ubiquitous mixed ionic/electronic conducting polymer blend, resulting from its wide commercial availability, biocompatibility and straightforward processing. However, when implemented in ion-gated transistors, PEDOT:PSS has two key drawbacks. First, it is intrinsically doped with positive charges (holes) due to the negatively charged PSS backbone. As a result, transistors based on this material operate by default in the ON state unless they are switched to the OFF state with an applied gate potential V_G (this is the so-called depletion-mode operation of a transistor, whose transfer characteristic is shown in Fig. 1b, red curve). A default ON state leads to both relatively high power consumption as well as device-to-device crosstalk due to the transmission of signals when $V_G = 0$ V. Second, the high areal

capacitance of PEDOT:PSS leads to slow charging times, limiting the operating speed of the transistors.

The authors have overcome both problems by combining an internal ion-gated organic electrochemical transistor (IGT) architecture, based on previous work[3], with a common de-doping reagent for PEDOT:PSS, polyethylene-imine. The IGT architecture results in a faster device response due to the inclusion of the electrolyte in the device channel to avoid diffusion-limited ionic transport, as well as the use of a low-capacitance gate that reduces the total RC charging time of the device (Fig. 1a). The de-doping reagent lowers the threshold potential to effectively tune the device to its OFF state when no gate voltage is applied — the device thus operates in enhancement mode, and its transfer characteristic is shifted with respect to V_G (as shown in Fig. 1b, green curve). This means that the IGT channel has high intrinsic resistance when $V_G = 0$ V, ensuring that stray signals are blocked from the surrounding circuitry.