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Large-scale chemical assembly of atomically thin transistors and circuits

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Next-generation electronics calls for new materials beyond silicon, aiming at increased functionality, performance and scaling in integrated circuits. In this respect, two-dimensional gapless graphene and semiconducting transition-metal dichalcogenides have emerged as promising candidates due to their atomic thickness and chemical stability. However, difficulties with precise spatial control during their assembly currently impede actual integration into devices. Here, we report on the large-scale, spatially controlled synthesis of heterostructures made of single-layer semiconducting molybdenum disulfide contacting conductive graphene. Transmission electron microscopy studies reveal that the single-layer molybdenum disulfide nucleates at the graphene edges. We demonstrate that such chemically assembled atomic transistors exhibit high transconductance (10 μS), on–off ratio ($\sim 10^6$) and mobility ($\sim 17\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$). The precise site selectivity from atomically thin conducting and semiconducting crystals enables us to exploit these heterostructures to assemble two-dimensional logic circuits, such as an NMOS inverter with high voltage gain (up to 70).

Moore's Law projects that integrated electronics will soon require sub-10 nm transistors. With silicon, this will be extremely challenging, because the thickness of the transistor's channel will become greater than the channel length, ultimately leading to difficult electrostatic control via the transistor gate[1]. The chemical syntheses of nanomaterials such as inorganic nanowires[2–4] and carbon nanotubes[5–7] have been aimed at addressing this issue, but using such materials in electrical devices requires precise placement and orientation using complex fabrication techniques[1,4,7,8]. Although great strides have been made, for example in the demonstration of a carbon nanotube computer[9], the fabrication required to create sophisticated electronic circuitry using these materials remains difficult or impractical. Recently, crystalline two-dimensional materials, with their ultimate atomic thickness, have shown promise as an elegant solution to the problematic scaling of silicon transistors. Graphene, the first widely studied two-dimensional crystal, is a semi-metal with a massless carrier dispersion, high mobility and easily tunable Fermi level. Single-layer graphene lacks an electronic bandgap, rendering it unsuitable for a transistor channel (as it cannot be turned 'off' easily), but its excellent conductive properties make it ideal for the interconnections and wiring of next-generation devices[10–13].

Semiconducting transition-metal dichalcogenides (TMDCs) such as molybdenum disulfide (MoS_2) have recently found success in a single-layer transistor[14,15]. While early works using single-layer TMDCs relied on the 'Scotch tape' method of micromechanical exfoliation, considerable efforts have established the chemical vapour deposition (CVD) of a range of TMDCs[16–20]. For example, CVD lateral heterostructures that include two different TMDCs have been used to create atomically sharp p–n junctions[21,22]. Lateral heterostructures using wide-gap insulators and conductors, hexagonal boron nitride (h-BN) and graphene have also been grown[23,24], but the spatially controlled synthesis of conductor–semiconductor heterostructures—a necessary step towards achieving full atomically thin circuitry—has not yet been demonstrated.

Here, we demonstrate the chemical assembly of heterojunctions using graphene–MoS_2–graphene heterostructures, as shown in Fig. 1a. Unlike previous reports that rely on transferring and physically assembling transistors using these two-dimensional crystals[25–29], we chemically grow these transistors on a large scale. By effectively injecting current from the graphene through the MoS_2, we demonstrate an NMOS inverter for logic operations using such heterostructure transistors.

Graphene–MoS_2 growth and optical characterization

To chemically assemble our heterostructures, single-layer graphene was first transferred onto a silica substrate (large-scale growth and transfer techniques for graphene are now common[10,11]). Patterns of channels (we have chosen a grid) were defined using oxygen plasma. The graphene on silica was then placed into a quartz tube for seed-promoted CVD growth of single-layer MoS_2. The fabrication on graphene before this growth results in dangling bonds and lithographic residues, causing a high density of MoS_2 nucleation at the edges. The lack of new chemical bonding and crystalline mismatch between these two crystals results in nanometre-scale overlap junctions between the two atomic crystals. Preferential growth within the SiO_2 channels results in the merging of individual domains, which form a continuous, polycrystalline single layer of MoS_2, consistent with the observations made with large-area chemical vapour growth on bare substrates[16,19,20] (see Methods for additional growth details).

Using solid precursors, we successfully grew heterostructures with millimetre-scale coverage, as shown in Fig. 1b, where the uniform single-layer MoS_2 can be observed within defined channels in the etched graphene. With optical microscopy, triangular MoS_2 grains are observed along the graphene, indicating that the edge serves as a site for crystal nucleation (see Supplementary Fig. 1 for

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Nanoscale topographical control of capillary assembly of nanoparticles

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Predetermined and selective placement of nanoparticles onto large-area substrates with nanometre-scale precision is essential to harness the unique properties of nanoparticle assemblies, in particular for functional optical and electro-optical nanodevices. Unfortunately, such high spatial organization is currently beyond the reach of top-down nanofabrication techniques alone. Here, we demonstrate that topographic features comprising lithographed funnelled traps and auxiliary sidewalls on a solid substrate can deterministically direct the capillary assembly of Au nanorods to attain simultaneous control of position, orientation and interparticle distance at the nanometre level. We report up to 100% assembly yield over centimetre-scale substrates. We achieve this by optimizing the three sequential stages of capillary nanoparticle assembly: insertion of nanorods into the traps, resilience against the receding suspension front and drying of the residual solvent. Finally, using electron energy-loss spectroscopy we characterize the spectral response and near-field properties of spatially programmable Au nanorod dimers, highlighting the opportunities for precise tunability of the plasmonic modes in larger assemblies.

The design of nanoparticle clusters and their deterministic spatial arrangement are core opportunities[1] as well as challenges[2] for nanotechnology. Nanofabrication by thin-film deposition, lithography and etching often produces nanostructures with grains and defects, which reduces their structural quality. In contrast, bottom-up assembly harnesses the superior and unique physico-chemical properties of semiconductor nanowires[3], carbon nanotubes[4], nanodiamonds[5] and colloidal quantum dots[6], as well as metallic nanoparticles with tailored composition[7], geometry[8] and functionalization[9,10]. In particular, single-crystal and geometrically perfect metallic colloids are excellent building blocks for low-loss[11] and strongly coupled plasmonic systems[12]. Fabrication approaches using DNA[13] as both a linker and scaffold have demonstrated ångström-level accuracy in self-assembling clusters of molecules[14] and nanoparticles[15–17]. Yet building functional devices with a precise architecture additionally requires such a high degree of organization to be reconciled with a correspondingly accurate spatial placement of the nanocomponents over large areas[18]. Capillary assembly of nanoparticles[19,20] may represent an effective technique for this purpose[21]. Capillary assembly achieves selective delivery of individual nanoparticles into suitable target sites when performed on substrates templated through topographical patterning and surface-chemical conditioning (Fig. 1)[22,23]. Thereby, capillary assembly of nanoparticles combines the complementary advantages of the chemical synthesis of nanoparticles[2,15] with those of top-down nanofabrication, ideal for the precise definition of topographic features arbitrarily distributed over large surfaces.

Capillary assembly of colloids is attracting increasing attention[24] and has witnessed several variations[25–27] and extensions[28,29]. Yet, in spite of recent relevant insights[30,31], complete understanding of the dynamics and the parametric dependence of its performance is still elusive. Here, we identify and investigate three distinct sequential stages in the dynamics of the capillary assembly of nanoparticles—namely insertion, resilience and drying—that encompass the trajectory of single nanoparticles from the initial colloidal suspension to the final placement onto topographical substrates. We demonstrate that each stage significantly and distinctively affects the cumulative yield of the assembly process, and have designed effective traps geometrically tailored in all three dimensions to achieve an optimal assembly performance.

Sequential stages of capillary assembly of nanoparticles

In the capillary assembly of nanoparticles, high assembly yield is correlated to dense nanoparticle packing in the accumulation zone (Fig. 1)[22]. Dense packing drastically quenches the Brownian motion of the nanoparticles, increasing the probability of nanoparticle sequestration into topographical traps. Deprived of thermal positional fluctuations, the nanoparticles in the accumulation zone are dragged across the underlying substrates exclusively by the receding motion of the triple contact line. For the Au nanorods used in this work (see Methods and Supplementary Fig. 1), anisotropic domains with smectic order extending over thousands of nanorods are visible from the surface of the accumulation zone (Supplementary Fig. 2a–e)[30]. Within the accumulation zone, multiple microscopic domains with short-range order are formed in a few nanorod monolayers adjacent to the substrate surface (Supplementary Fig. 2c,f). Each domain contains on average a few tens of uniformly aligned nanorods, and the domains span the entire range of orientations (Supplementary Fig. 3). The domains of nanorods in contact with the substrate prompt a new interpretation of prior experimental observations—specifically, the increase of assembly yield reported for an increased extension of the

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A dressed spin qubit in silicon

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Coherent dressing of a quantum two-level system provides access to a new quantum system with improved properties—a different and easily tunable level splitting, faster control and longer coherence times. In our work we investigate the properties of the dressed, donor-bound electron spin in silicon, and assess its potential as a quantum bit in scalable architectures. The two dressed spin-polariton levels constitute a quantum bit that can be coherently driven with an oscillating magnetic field, an oscillating electric field, frequency modulation of the driving field or a simple detuning pulse. We measure coherence times of $T_{2\rho}^{*} = 2.4$ ms and $T_{2\rho}^{\mathrm{Hahn}} = 9$ ms, one order of magnitude longer than those of the undressed spin. Furthermore, the use of the dressed states enables coherent coupling of the solid-state spins to electric fields and mechanical oscillations.

Coherent dressing of a quantum two-level system has been demonstrated on a variety of systems, including atoms[1], self-assembled quantum dots[2], superconducting quantum bits[3] and nitrogen-vacancy (NV) centres in diamond[4]. In this context 'dressing' means that an electromagnetic driving field coherently interacts with the quantum system, so that the eigenstates of the driven system are the entangled states of the photons and the quantum system. For the case of a single spin in a static magnetic field B_0 that is driven with an oscillating magnetic field B_1, this means that the eigenstates are no longer the spin-up and spin-down states, but the symmetric and antisymmetric superpositions of these states with the driving field (Fig. 1b).

The dressed system possesses a level splitting proportional to the driving strength, and can therefore be modified dynamically and tuned to be in resonance with other quantum systems[4–6]. Furthermore, the continuous driving decouples the spin from background magnetic field noise. Even in highly coherent systems such as trapped atoms, coherence times can be improved by two orders of magnitude by dressing the states[7]. Finally, the change in quantization axis unlocks new ways of operating on a dressed qubit. A dressed qubit can be controlled by changes in the bare spin Larmor frequency, which allows manipulation using electric fields and strain via the hyperfine coupling in donor systems[8,9]. This opens up the possibility of coupling spins to the motion of a mechanical oscillator when the transition frequency between dressed states becomes comparable to the oscillator's frequency[10,11].

As a result of these benefits, it has been proposed that dressed states be used for quantum gates and memories for quantum computing[7,12,13]. In these proposals, the focus was on optically dressed qubits in trapped atomic ions, because dressing a qubit fundamentally requires a high ratio between the driving field and the intrinsic resonance linewidth, most easily achieved in optics and trapped ions. Here we demonstrate a microwave (MW)-dressed spin qubit in the solid state, using a highly coherent ^{31}P-donor-bound electron in silicon[14]. We demonstrate that the use of dressed states, compared with that of bare spin states, has several advantages for quantum computation.

The ^{31}P donor in silicon constitutes a natural two-qubit system, in which both the electron (indicated with $|{\downarrow}\rangle$ or $|{\uparrow}\rangle$) and the nuclear ($|{\Downarrow}\rangle$ or $|{\Uparrow}\rangle$) spin states can be controlled coherently by a magnetic field B_1 oscillating at specific electron-spin resonance (ESR) and nuclear magnetic resonance frequencies. Figure 1a shows a device similar to the one measured. It consists of a single ^{31}P donor in an isotopically purified ^{28}Si epilayer[15], implanted[16] next to the island of a single-electron transistor (SET). The SET is formed by biasing a set of electrostatic gates (yellow), whereas donor gates (pink) are used to tune the electrochemical potential μ of the donor with respect to that of the SET island. The device is cooled down to $T_{\mathrm{electron}} \approx 100$ mK, and subjected to a static magnetic field $B_0 = 1.55$ T. High-fidelity, single-shot electron-spin readout as well as initialization of the donor electron spin into the $|{\downarrow}\rangle$ state is achieved via spin-dependent tunnelling of the electron to the SET island[17,18]. Coherent spin control is achieved with an oscillating magnetic field B_1 delivered to the donor through an on-chip, broadband, nanoscale antenna[19] (blue in Fig. 1a).

Dressing the electron spin

Figure 1b shows the energy-level diagram of the electron-spin subsystem. Naturally, we would draw the energy levels in the $|{\uparrow}\rangle$—$|{\downarrow}\rangle$ basis, which corresponds to the spin picture, with electron-spin transition frequency ν_{e}. Alternatively, we can draw them in the dressed $|N+1\rangle$—$|N\rangle$ basis, where N is the total number of excitations in the system. The state $|N\rangle$ then consists of the two degenerate states $|{\downarrow}, n\rangle$ and $|{\uparrow}, n-1\rangle$, where n is the number of resonant photons in the driving field. For a non-zero spin–photon coupling, the dressed levels are split into the entangled $|+, N\rangle = (1/\sqrt{2})(|{\downarrow}, n\rangle + |{\uparrow}, n-1\rangle)$ and $|-, N\rangle = (1/\sqrt{2})(|{\downarrow}, n\rangle - |{\uparrow}, n-1\rangle)$ states, which differ in energy by the Rabi frequency $\Omega_{\mathrm{R}} = (1/2)\gamma_{\mathrm{e}}B_1$ where $\gamma_{\mathrm{e}} = 28$ GHz/T is the gyromagnetic ratio of the electron and B_1 is the amplitude of the oscillating driving field.

We can define the dressed spin states as the basis states of a new qubit, the dressed qubit. Here the states $|-\rangle$ and $|+\rangle$ act as the computational basis states. We have omitted N, the number of excitations in the system, as the electron is dressed by a classical driving field, in

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PRINTING TECHNOLOGY

Ultrathin high-resolution flexographic printing using nanoporous stamps

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Since its invention in ancient times, relief printing, commonly called flexography, has been used to mass-produce artifacts ranging from decorative graphics to printed media. Now, higher-resolution flexography is essential to manufacturing low-cost, large-area printed electronics. However, because of contact-mediated liquid instabilities and spreading, the resolution of flexographic printing using elastomeric stamps is limited to tens of micrometers. We introduce engineered nanoporous microstructures, comprising polymer-coated aligned carbon nanotubes (CNTs), as a next-generation stamp material. We design and engineer the highly porous microstructures to be wetted by colloidal inks and to transfer a thin layer to a target substrate upon brief contact. We demonstrate printing of diverse micrometer-scale patterns of a variety of functional nanoparticle inks, including Ag, ZnO, WO$_3$, and CdSe/ZnS, onto both rigid and compliant substrates. The printed patterns have highly uniform nanoscale thickness (5 to 50 nm) and match the stamp features with high fidelity (edge roughness, ~0.2 μm). We derive conditions for uniform printing based on nanoscale contact mechanics, characterize printed Ag lines and transparent conductors, and achieve continuous printing at a speed of 0.2 m/s. The latter represents a combination of resolution and throughput that far surpasses industrial printing technologies.

INTRODUCTION

For centuries, innovations in printing technologies have gone hand-in-hand with advances in communication, education, and industrialization. Relief printing, which was invented in China using hand-carved woodblock stamps in ~200 CE (*1*), involves loading of ink onto raised stamp structures, followed by transfer to the target substrate by mechanical contact. The invention of metal relief printing stamps in the year ~1230 enabled mass production of books (*2*), and the invention of rubber stamps in the 1860s enabled roll-to-roll production of high-quality graphics (*3*). This latter process is commonly called flexography.

Further breakthroughs in printing technologies are now essential to scalable manufacturing of electronic devices (*4*, *5*) in large-area and unconventional formats, such as on windows, contact lenses, ultrathin membranes, and flexible films. Low-cost printed electronics are also central to the vision of an "internet of things," encompassing ubiquitous connected devices and means of tracking everyday objects, including medicines, foods, and products during transportation and use (*6*). However, the inability to print electronic materials with micrometer-scale resolution (that is, minimum feature size of 1 to 10 μm) at high throughput is a major roadblock in this pursuit (*7*–*9*). For example, thin-film transistors with smaller lateral dimensions have higher bandwidth and on/off switching speed along with reduced parasitic capacitance, operation voltage, and power consumption. Narrower and thinner conductive lines are also essential to realize metal grid electrodes with improved transparency, and high-resolution displays having micrometer-scale transistor backplane features.

In addition to flexography (*10*, *11*), the mainstream methods for printing electronic materials include inkjet (*12*–*14*), screen (*15*–*18*), and gravure (intaglio) (*19*–*22*) printing. The suitability of each method for a particular application is determined by its resolution, throughput, and materials compatibility, among other attributes. For example, inkjet printing is compatible with many colloidal and polymer inks, yet the size of the droplet that can be ejected from the nozzle aperture is, at present, no less than 10 to 20 μm (*23*). Flexography is also compatible with a wide variety of substrates and inks, but its resolution is limited to 50 to 100 μm (*7*–*11*) despite the capability to manufacture rubber stamps with micrometer and submicrometer feature sizes (*24*). For high-quality flexographic printing, the liquid films need to be thin enough to avoid spreading out from the contact area when compressed, yet such thin films tend to dewet from the stamp surface due to hydrodynamic instability. Higher-resolution printing technologies have been invented and demonstrated, including microcontact (*25*), nanotransfer (*26*), electrohydrodynamic (*27*), and dip-pen (*28*, *29*) methods, yet these lack the throughput and versatility of the mainstream methods.

To enable the next generation of relief printing for electronics manufacturing, we conceived a microstructured nanoporous stamp material that enables ultrathin, high-resolution direct printing of colloidal inks. The stamp is fabricated using patterned aligned carbon nanotubes (CNTs) conformally coated with a thin polymer, such that its porosity, mechanical properties, and surface chemistry enable capillary-driven loading of ink and nanoscale contact-mediated ink transfer. We show that diverse patterns of a variety of electronic nanomaterials, including Ag, ZnO, WO$_3$ nanoparticles (NPs), and CdSe/ZnS quantum dots (QDs), can be directly printed with micrometer-scale resolution and that the process can be scaled to industrially relevant throughput.

RESULTS

Engineering CNT microstructures as a nanoporous stamp

In Figure 1A we show a schematic description of the printing process using nanoporous stamps, along with exemplary printed materials. First, the polymer-CNT stamp is loaded with an NP-based ink via immersion or spin coating, causing the ink to be drawn into the nanoscale pores within each microstructure (fig. S1) by capillary wicking.

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Memristors with diffusive dynamics as synaptic emulators for neuromorphic computing

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The accumulation and extrusion of Ca^{2+} in the pre- and postsynaptic compartments play a critical role in initiating plastic changes in biological synapses. To emulate this fundamental process in electronic devices, we developed diffusive Ag-in-oxide memristors with a temporal response during and after stimulation similar to that of the synaptic Ca^{2+} dynamics. *In situ* high-resolution transmission electron microscopy and nanoparticle dynamics simulations both demonstrate that Ag atoms disperse under electrical bias and regroup spontaneously under zero bias because of interfacial energy minimization, closely resembling synaptic influx and extrusion of Ca^{2+}, respectively. The diffusive memristor and its dynamics enable a direct emulation of both short- and long-term plasticity of biological synapses, representing an advance in hardware implementation of neuromorphic functionalities.

Complementary metal–oxide–semiconductor circuits have been employed to mimic synaptic Ca^{2+} dynamics, but three-terminal devices bear limited resemblance to bio-counterparts at the mechanism level and require significant numbers and complex circuits to simulate synaptic behaviour[1–3]. A substantial reduction in footprint, complexity and energy consumption can be achieved by building a two-terminal circuit element, such as a memristor directly incorporating Ca^{2+}-like dynamics. Various types of memristor based on ionic drift (drift-type memristor)[4–8] have recently been utilized for this purpose in neuromorphic architectures[9–15]. Although qualitative synaptic functionality has been demonstrated, the fast switching and non-volatility of drift memristors optimized for memory applications do not faithfully replicate the nature of plasticity. Similar issues also exist in metal–oxide–semiconductor-based memristor emulators[16–18], although they are capable of simulating a variety of synaptic functions including spike-timing-dependent plasticity (STDP). Recently, researchers adopted second-order drift memristors to approximate the Ca^{2+} dynamics of chemical synapses by utilizing thermal dissipation[19] or mobility decay[20], which successfully demonstrated STDP with non-overlapping spikes and other synaptic functions, representing a significant step towards bio-realistic synaptic devices. This approach features repeatability and simplicity, but the significant differences of the physical processes from actual synapses limit the fidelity and variety of desired synaptic functions. A device with similar physical behaviour to the biological Ca^{2+} dynamics would enable improved emulation of synaptic function and broad applications to neuromorphic computing. Here we report such an emulator, which is a memristor based on metal atom diffusion and spontaneous nanoparticle formation, as determined by *in situ* high-resolution transmission electron microscopy (HRTEM) and nanoparticle dynamics simulations. The dynamical properties of the diffusive memristors were confirmed to be functionally equivalent to Ca^{2+} in bio-synapses, and their operating characteristics were experimentally verified by demonstrating both short- and long-term plasticity, including synaptic functions that have not been unambiguously demonstrated previously.

The diffusive memristor illustrated in Fig. 1a consists of two Pt or Au inert electrodes sandwiching a switching layer of a dielectric film with embedded Ag nanoclusters (Methods). X-ray photoelectron spectroscopy revealed that the Ag was metallic, which was further confirmed by HRTEM micrographs showing Ag nanocrystals in SiO_xN_y:Ag (Supplementary Figs 1 and 2). These devices are similar to electrochemical metallization memory[21–26] cells in terms of utilizing mobile species of noble metals, but they differ substantially in terms of the structural and electrical biasing symmetry, metal concentration and profile, and transient switching behaviour. An applied voltage above an apparent threshold abruptly switched the device to a conductance state limited by an external compliance current (Fig. 1b). To demonstrate that the device spontaneously relaxed back to an insulating configuration on removing the bias (without applying an opposite polarity voltage), repeatable I–V loops with only positive applied voltages were used in collecting the data in Fig. 1b. Symmetric hysteresis loops were observed with the opposite polarity bias (Supplementary Fig. 3), showing that the threshold switching is unipolar in nature and significantly different from non-volatile drift-type memristors, especially in the OFF-switching process. The micro-devices represented by Fig. 1a have an area of 10 μm × 10 μm and nano-devices with an area of 100 nm × 100 nm exhibited similar switching behaviours (Supplementary Fig. 4). The resistance ratio between the conducting and insulating states was five orders of magnitude in SiO_xN_y:Ag and over ten orders in HfO_x:Ag devices, the highest reported in threshold switching devices so far[27–30]. The volatile switching had sharp turn-on slopes of $\sim$10 mV decade^{-1} in MgO_x:Ag and SiO_xN_y:Ag, and an extraordinary $\sim$1 mV decade^{-1} in HfO_x:Ag, the sharpest demonstrated to date[27–30]. The high current capability and large resistance ratio enable diffusive memristors to be utilized as

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REVIEW ARTICLE

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Metal oxides for optoelectronic applications

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Metal oxides (MOs) are the most abundant materials in the Earth's crust and are ingredients in traditional ceramics. MO semiconductors are strikingly different from conventional inorganic semiconductors such as silicon and III–V compounds with respect to materials design concepts, electronic structure, charge transport mechanisms, defect states, thin-film processing and optoelectronic properties, thereby enabling both conventional and completely new functions. Recently, remarkable advances in MO semiconductors for electronics have been achieved, including the discovery and characterization of new transparent conducting oxides, realization of p-type along with traditional n-type MO semiconductors for transistors, p–n junctions and complementary circuits, formulations for printing MO electronics and, most importantly, commercialization of amorphous oxide semiconductors for flat panel displays. This Review surveys the uniqueness and universality of MOs versus other unconventional electronic materials in terms of materials chemistry and physics, electronic characteristics, thin-film fabrication strategies and selected applications in thin-film transistors, solar cells, diodes and memories.

The discovery of hydrogenated amorphous silicon (a-Si:H) exposed new frontiers in large-area electronics[1]. This semiconductor is a key material for thin-film transistors (TFTs) used in display backplane electronics; yet, its low carrier mobility (~0.5–1.0 $cm^2 V^{-1} s^{-1}$), optical opacity, poor current-carrying capacity and modest mechanical flexibility present challenges for future applications. To overcome such limitations, researchers have explored the use of metal oxides (MOs), which, compared with crystalline silicon and other III–V semiconductors, exhibit unique properties, including excellent carrier mobilities even in the amorphous state, mechanical stress tolerance, compatibility with organic dielectric and photoactive materials, and high optical transparency. Furthermore, high-quality electronic-grade MO thin films are accessible using vapour- and solution-phase methodologies in near-ambient conditions (~25 °C under air), widening their applicability to high-value products such as inexpensive circuits, and to flexible organic light-emitting diode (OLED) displays and solar cells on plastic substrates.

The first MO TFT using semiconducting SnO_2 was reported in 1964 (ref. 2), yet it was the more recent work by Hosono that stimulated extensive research and increases in performance[3]. MO TFTs based on polycrystalline MO materials such as indium oxide (In_2O_3; ref. 4), tin oxide (SnO_2; ref. 5) and zinc oxide (ZnO; ref. 6) were reported. The first amorphous oxide semiconductors (AOSs), whose compatibility with large-area fabrication processes make them technologically appealing, were synthesized in 1954 (ref. 7), yet there was little interest in their properties until Hosono's work on In–Ga–Zn oxide (IGZO) sparked worldwide attention in 2003 (ref. 8). IGZO TFTs have since been commercialized in active-matrix displays, joining the widely used transparent conducting oxide (TCO) electrode material, tin-doped indium oxide (ITO). The unique properties of MOs, their synthesis and their use in optoelectronic devices are described in this Review.

Optoelectronic properties of metal oxides

Carrier mobility is a key metric of semiconductor performance. Traditional band theory descriptions of transport in semiconductors, including wide-gap ionic MOs, represent electronic structure in reciprocal space, with the conduction band minimum (CBM) and the valence band maximum (VBM) curvatures and dispersions determining the electron and hole effective masses, respectively. Smaller effective masses mean greater CBM and VBM hybridization, affording larger carrier mobilities, all other factors being equal. Note that transport in MOs is very different from that in Si semiconductors, where hybridized sp^3 σ-bonding and sp^3 σ*-antibonding states define the VBM and CBM, respectively[9]. In the oxides of interest here, the VB is typically composed of occupied 2*p* O anti-bonding states, and the CB primarily of unoccupied *ns* metal bonding states (Fig. 1a)[8]. The spatially extended, spherically symmetrical *ns*-orbital CBM affords small electron effective masses and efficient electron transport even in the amorphous state, because the spherically symmetrical metal *s*-orbital overlap is minimally affected by lattice distortions. In contrast, the spatially directional Si sp^3 σ states experience dramatically reduced carrier mobilities in the amorphous (a-Si) state. Thus, the electron mobilities of AOSs are often similar to those of the corresponding single crystals[8], and the subgap distributions of the density of states (DOS) between amorphous covalent (such as a-Si) and amorphous oxide (such as a-IGZO) semiconductors differ greatly (Fig. 1b)[9]. The subgap DOS in a-IGZO is 10–100 times smaller than in a-Si:H[10,11].

Many MO (semi)conductors have energy gaps greater than 3 eV, hence, they are transparent in the visible spectrum. Although from a traditional band-structure perspective, high conductivity and optical transparency seem contradictory[12]; in many (semi)conducting MOs, strong interactions between the O 2*p*- and metal *ns*-orbitals produce a band structure characterized by high free-electron mobility (μ_e) due to the low effective mass and by low optical absorption due to the large bandgap (Burstein-Moss shift) and the low DOS in the CB (ref. 12). However, this unique electronic structure causes a dearth of p-type MOs, as hole conduction is hampered by localized O 2*p* orbitals and deep VBM levels where holes are trapped by O ions[12,13]. Band-structure and band-energy modifications are key strategies for the design of p-type MOs, and electrical, X-ray and photoemission experiments argue that greater VBM dispersion is

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Mixed-dimensional van der Waals heterostructures

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The isolation of a growing number of two-dimensional (2D) materials has inspired worldwide efforts to integrate distinct 2D materials into van der Waals (vdW) heterostructures. Given that any passivated, dangling-bond-free surface will interact with another through vdW forces, the vdW heterostructure concept can be extended to include the integration of 2D materials with non-2D materials that adhere primarily through non-covalent interactions. We present a succinct and critical survey of emerging mixed-dimensional (2D + *n*D, where *n* is 0, 1 or 3) heterostructure devices. By comparing and contrasting with all-2D vdW heterostructures as well as with competing conventional technologies, we highlight the challenges and opportunities for mixed-dimensional vdW heterostructures.

In 2004, the isolation of graphene on an insulating surface[1] gave birth to a new era of atomically thin materials in solid-state electronics, which ultimately led to the search for additional two-dimensional materials[2]. The emergence of both structural and electronic variety in van der Waals (vdW)-bonded layered materials has opened new avenues for fundamental scientific studies and applied device designs. As a consequence, several combinations of distinct 2D layers have been assembled to create vdW heterostructures with varying functionalities[3–8]. These all-2D vdW heterostructures offer unique properties such as gate-tunability, imbuing them with potentially new functionality compared with conventional devices, as summarized in several recent reviews[9–11]. But it remains a challenge to produce entire families of 2D materials and their heterostructures over large areas with high electronic quality. Furthermore, control of doping type, carrier concentration and stoichiometry remain outstanding challenges for most 2D materials, limiting the scope and progress of all-2D vdW heterostructures[2,11,12].

Van der Waals interactions are not limited to interplanar interactions in layered materials. Indeed, any passivated, dangling-bond-free surface interacts with another by vdW forces. Consequently, any layered 2D material can be integrated with an array of materials of different dimensionality to form mixed-dimensional vdW heterostructures. Such combinations of 2D + *n*D ($n = 0$, 1 and 3) materials have begun to emerge and represent a much broader class of vdW heterostructures for further study. In this Review, we present a survey of mixed-dimensional vdW heterostructures, with particular emphasis on their applicability in solid-state devices. We first present a general categorization of mixed-dimensional heterostructures and introduce the classes of materials involved. We then discuss the physics of charge transport and band alignments at mixed-dimensional interfaces, while also highlighting the relevant chemistry and synthetic routes. Finally, we discuss the applications of mixed-dimensional heterostructures in the context of solid-state devices and present an outlook on their future integration into mainstream technologies.

Structure, physical properties and fabrication

Although mixed-dimensional vdW heterostructures have been investigated over the past two decades in organic photovoltaics and light-emitting diodes, the focus here is on combinations involving at least one 2D component (Fig. 1a). In earlier examples of mixed-dimensional vdW heterostructures prior to the advent of 2D materials, the interface was often extremely complex and poorly defined, making it difficult to quantify the active junction area and consequently the physical properties associated with the junction. In addition to the complex geometry, the junction interface is physically and electronically buried in most examples that do not involve 2D materials, such as organic heterojunctions[13] and composites of nanowires or nanotubes[14] with 3D or 0D materials. In contrast, a continuous, atomically thin sheet of material presents a better-defined interface geometry that is amenable to quantitative characterization. Furthermore, the low density of electronic states and lower values of relative permittivity in 2D materials (as compared with the bulk) render them semi-transparent to applied electric fields normal to the 2D plane. Consequently, the junction interface can be modulated as a function of an applied gate voltage, leading to fundamentally new device phenomena in addition to providing another knob for tuning device properties.

Hence, we discuss here three distinct mixed-dimensional heterostructure geometries, namely 2D–0D, 2D–1D and 2D–3D (Fig. 1b–d). The 2D components such as graphene, hexagonal boron nitride (h-BN) and transition-metal dichalcogenides (TMDCs) (Fig. 1a) have been thoroughly investigated[2,9,10,12,15,16]. The class of 0D materials primarily consists of fullerenes[17], small organic molecules[18] and quantum dots[19], while the 1D class includes semiconducting single-walled carbon nanotubes (SWCNTs; ref. 20), semiconducting organic polymers[18] and inorganic semiconductor nanowires[21]. Finally, our discussion of the 3D materials class will focus on crystalline bulk Si, Ge, III–V and II–VI semiconductors as well as semiconducting amorphous oxides (such as indium gallium zinc oxide (IGZO)[22] and amorphous Si). Figure 2 depicts examples of each materials class.

Physical properties. In contrast to conventional, epitaxially grown heterostructures, the interface in a mixed-dimensional vdW heterostructure is more complex and less constrained, as there is no need for lattice matching. Furthermore, in addition to the usual discontinuity in band structure and resulting potential energy barriers, the density of states (DOS) also undergoes an abrupt transition, which has several observable implications, such as additional resistance at the junction that results from the change in the number of conductance channels.

Typically, point and line defects in a covalently or ionically bonded interface are the source of trap states, which have energy levels within the gap of the constituent semiconductors, giving rise to Fermi-level pinning and non-radiative carrier recombination. Although most vdW interfaces (including many of the all-2D heterostructures) are immune to this class of defects, they are

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Flexible non-volatile optical memory thin-film transistor device with over 256 distinct levels based on an organic bicomponent blend

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Organic nanomaterials are attracting a great deal of interest for use in flexible electronic applications such as logic circuits, displays and solar cells. These technologies have already demonstrated good performances, but flexible organic memories are yet to deliver on all their promise in terms of volatility, operational voltage, write/erase speed, as well as the number of distinct attainable levels. Here, we report a multilevel non-volatile flexible optical memory thin-film transistor based on a blend of a reference polymer semiconductor, namely poly(3-hexylthiophene), and a photochromic diarylethene, switched with ultraviolet and green light irradiation. A three-terminal device featuring over 256 (8 bit storage) distinct current levels was fabricated, the memory states of which could be switched with 3 ns laser pulses. We also report robustness over 70 write–erase cycles and non-volatility exceeding 500 days. The device was implemented on a flexible polyethylene terephthalate substrate, validating the concept for integration into wearable electronics and smart nanodevices.

Although silicon-based technology is still effectively leading today's electronics industry, the development of high-performance organic semiconducting nanomaterials has been the subject of important research efforts in the past two decades[1–3]. Such materials are undoubtedly an interesting alternative, because their properties can be tuned readily via ad hoc chemical synthesis, and they can be fabricated using mild processing from solution using approaches that can be scaled up and applied to 'soft' substrates, making them ideal candidates for the low-cost fabrication of large-area electronic devices. They have shown exceptional versatility, enabling integration on flexible and/or transparent substrates for a new generation of electronics[4–7]. Among the plethora of applications of semiconducting organic materials and more generally of π-conjugated (macro)molecules, memories have attracted particular interest because they combine high switching ratios[8–10] and long retention times[11], as well as low operating voltages[12–14] and the possibility to be integrated onto flexible substrates[15–18].

To increase the data storage capabilities of electronic devices (hard drives, random access memories and so on), the most popular approaches so far have relied on a continuous scaling down to enable the integration of an increasing number of memory cells per unit area. These strategies have shown their limits, as scaling down is hampered by photolithography, and fabrication complexity has increased dramatically over the years[19,20]. An alternative method is based on the development of memory cells with increased storage capabilities, that is, multilevel memories. In 1 bit storage devices, a finite yet limited degree of volatility is not detrimental to the overall storage capacity as long as the two states, typically represented by a current maximum and minimum, are still distinguishable. The main challenge is to obtain the highest possible difference in current between an on state and an off state. When multilevel memories are considered, the problem shifts dramatically to ensuring the stability of the states, as each state will necessarily be close to others. In a 4 bit memory cell (16 current levels), for example, a one order of magnitude difference between each level is not achievable, because this would mean a switching ratio as high as 10^{15}. Importantly, all methods where a high switching ratio is simply based on a threshold voltage shift (that is, not characterized by a change in charge carrier mobility or current), with the 'read voltage' within a threshold voltage window, are prone to data loss and incorrect reading of the levels in multilevel storage[21,22].

Two- and three-terminal resistive switching memories based on polymers, organic small molecules and ferroelectric materials have demonstrated impressive switching ratios of up to 10^8 and low programming voltages[23–25]. Unfortunately, this approach relies on two stable states of polarization and is therefore not well suited to use in multilevel memories[26]. On the other hand, memories designed around electrets, that is, dielectric materials (usually polymers), or using polymer/electrolyte pairs exhibiting quasi-permanent electric charge or dipole polarization, have displayed the ability to perform as multilevel memories with different applied programming voltages. Although the observed switching ratios of over 10^8 have pushed them to the forefront of research on organic memories[27–30], their unacceptably high programming voltages (up to ±200 V) and, most importantly, their low retention times ($<10^4$ s) are still major obstacles towards their integration into everyday electronics[31,32]. Storing charges in a metal or semiconductor layer by exploiting the principle of a floating gate located within the dielectric can be achieved with metallic nanoparticles, with each particle counting as a charge-storage site that is independent and isolated from other sites. Although not yet extensively explored, this approach is relevant for the fabrication of multilevel memories with acceptable

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Origin and control of blinking in quantum dots

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Semiconductor nanocrystals offer an enormous diversity of potential device applications, based on their size-tunable photoluminescence, high optical stability and 'bottom-up' chemical approaches to self-assembly. However, the promise of such applications can be seriously limited by photoluminescence intermittency in nanocrystal emission, that is, 'blinking', arising from the escape of either one or both of the photoexcited carriers to the nanocrystal surface. In the first scenario, the remaining nanocrystal charge quenches photoluminescence via non-radiative Auger recombination, whereas for the other, the exciton is thought to be intercepted before thermalization and does not contribute to the photoluminescence. This Review summarizes the current understanding of the mechanisms responsible for nanocrystal blinking kinetics as well as core–shell engineering efforts to control such phenomena. In particular, 'softening' of the core–shell confinement potential strongly suppresses non-radiative Auger processes in charged nanocrystals, with successful non-blinking implementations demonstrated in CdSe–CdS core–thick-shell nanocrystals and their modifications.

Semiconductor nanocrystals (NCs), often referred to as quantum dots (QDs), are the most heavily studied nanoscale semiconductor structures. After almost 30 years of research, initiated by the pioneering efforts of Alexei Ekimov in semiconductor-doped glasses and Louis Brus in solutions[1–7], a solid theoretical framework has been built that now offers a high-level understanding for many of the electronic, optical, and transport properties of such nanocrystalline species.

By way of example, Fig. 1a displays a transmission electron micrograph of a PbS NC. From a chemist's perspective, one can think of this as just a big molecule with atoms organized in a bulk crystal structure (Fig. 1b), where current technology allows us to vary the size of these NCs in a controlled manner from 1 to 100 nm. From a physicist's perspective, on the other hand, a NC can be thought of as essentially a three-dimensional potential box that confines the otherwise free bulk motion of electrons and holes. This results in a discrete, size-dependent, energy-level pattern and thus NCs exhibit structured spectra arising from discrete optical excitations. What makes these NCs so spectacularly useful is that the absorption band edge, which is determined by optical transitions between the lowest electron and highest hole levels, can be shifted to higher energy by up to 1 eV simply by decreasing the NC size[4,8] (Fig. 1c). Size-dependent absorption spectra of PbS NCs[9] are shown in Fig. 1d, where the photoluminescence (PL) of the NCs redshifts only slightly from the first absorption peak (Fig. 1e) and thus corresponds closely to the NC bandgap. As a result, the size dependence of the absorption band edge maps nicely onto an equivalent size dependence of the PL frequencies, which therefore can be tuned over a broad range of wavelengths simply by changing the NC size (Fig. 1f).

Potential applications of nanocrystals

Size- and shape-controlled tunability of NC electronic, optical, and transport properties (Fig. 1d,f, size-dependent absorption and PL, respectively, of PbS NCs), combined with the ability to chemically and physically manipulate such 'freestanding' (that is, substrate-free) nanostructures with nanometre control and precision, open exciting new opportunities for the development of novel functional materials with a wide range of applications. In particular, such materials allow 'bottom-up' chemical approaches to assembly, whereby NCs can be positioned and assembled into two- and three-dimensional artificial super 'crystals'[10], custom-designed NC 'molecules'[11] and functional NC biomolecular conjugates[12].

We briefly mention three areas that represent particularly promising applications of NCs. The first involves the observation of tunable gain and stimulated emission in CdSe NC solids at room temperature[13], which highlights the potential for inexpensive NC lasers operating over a wide range of visible and near-infrared wavelengths. The second application concerns the successful labelling of biological molecules by NCs[14], which now paves the way for creating bright nanoscale semiconductor-based technologies for ultrasensitive imaging of cellular processes, neuronal brain networks, drug transport, and so on. Finally, in a more media-based direction, researchers from Samsung Electronics have demonstrated the first 4 inch full-colour QD display, which is brighter than liquid-crystal displays and yet consumes less than one-fifth of the power[15]. As an indication of the rapid progress for such applications, Samsung already has a commercial television product that utilizes InP-based QDs as green and red phosphors.

The above applications rely critically on a widely tunable emission spectrum with a relatively narrow emission line, whose properties are dominated by just one synthetically adjustable parameter, that is, the NC size (Fig. 1f). This spectacular control of optical tunability and the enormous chemical and physical flexibility of self-assembly also come together nicely with long-term optical stability. Specifically, unlike fluorescent dye molecules, NCs do not undergo irreversible photobleaching, with their unique PL properties surviving several billions of photon absorption events. However, while NCs do exhibit high PL quantum efficiencies in excess of 70% at room temperature, this still remains insufficient for some critical cryptography and signalling applications that rigorously require single-photon emitters. Indeed, though NCs do offer a crucial advantage over molecular chromophores as a result of their large absorption cross-sections and high peak fluorescence quantum yields, sub-unity average quantum efficiencies can be an intrinsic property of NCs (as discussed below), which leaves us with the as-yet-unfulfilled need for developing the perfect 'photon on-demand' QD emitter[16,17].

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Stochastic phase-change neurons

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Artificial neuromorphic systems based on populations of spiking neurons are an indispensable tool in understanding the human brain and in constructing neuromimetic computational systems. To reach areal and power efficiencies comparable to those seen in biological systems, electroionics-based and phase-change-based memristive devices have been explored as nanoscale counterparts of synapses. However, progress on scalable realizations of neurons has so far been limited. Here, we show that chalcogenide-based phase-change materials can be used to create an artificial neuron in which the membrane potential is represented by the phase configuration of the nanoscale phase-change device. By exploiting the physics of reversible amorphous-to-crystal phase transitions, we show that the temporal integration of postsynaptic potentials can be achieved on a nanosecond timescale. Moreover, we show that this is inherently stochastic because of the melt-quench-induced reconfiguration of the atomic structure occurring when the neuron is reset. We demonstrate the use of these phase-change neurons, and their populations, in the detection of temporal correlations in parallel data streams and in sub-Nyquist representation of high-bandwidth signals.

In biological neurons, a thin lipid-bilayer membrane separates the electrical charge inside the cell from that outside it, which, in conjunction with a number of electrochemical mechanisms, allows the membrane potential to be maintained[1]. The membrane potential is altered by the arrival of excitatory and inhibitory postsynaptic potentials through the dendrites of the neuron, and upon sufficient excitation of the neuron, an action potential is generated. The neuron is said to 'fire' or 'spike'. Emulation of these neuronal dynamics, including maintenance of the equilibrium potential, the transient dynamics and the process of neurotransmission, is fundamental in the realization of neuromorphic computing systems[2].

The complex neuronal dynamics captured in the Hodgkin–Huxley[3] model and in various threshold-based neuronal models[4] must often be simplified in hardware realizations for cost, performance and real-estate reasons. In doing so, the integration of the postsynaptic potentials and the subsequent firing events are the two most important dynamical components retained. However, emulating these by means of conventional CMOS circuits, such as current-mode, voltage-mode and subthreshold transistor circuits[5–9], is relatively complex and hinders seamless integration with highly dense synaptic arrays[10]. Moreover, conventional CMOS solutions rely on storing the membrane potential in a capacitor. Even with a drastic scaling of the technology node, realizing the capacitance densities measured in biological neuronal membranes[11] ($\sim$10 fF μm^{-2}) is challenging.

In addition to the deterministic neuronal dynamics, stochastic neuronal dynamics play a key role in signal encoding and transmission[12], for example in biological neuronal populations that represent and transmit sensory and motor signals. The stochastic behaviour can be attributed to a number of complex phenomena, such as the ionic conductance noise, the chaotic motion of charge carriers due to thermal noise, inter-neuron morphologic variabilities and background noise. This complexity has restricted the implementation of artificial noisy integrate-and-fire neurons in software simulations, despite their importance in bioinspired computation[13] and their intriguing applications in signal and information processing[14,15]. The relatively complex computational tasks, such as Bayesian inference, that stochastic neuronal populations can perform with collocated processing and storage render them attractive as a possible alternative to von-Neumann-based algorithms in future cognitive computers[16].

Recently, research has focused on exploiting the physics of nanometre-scale devices to emulate the biophysics of neuronal systems. Memristive devices—resistive elements that remember the history of the current that has flowed through them—are the most promising candidates in this regard[17]. Highly scalable and efficient memristive synapses have been demonstrated, in which bioinspired computation (including short-term and long-term potentiation and time-based plasticity[18–20]) could be realized using native device physics. However, realizations of artificial neurons using memristive devices have been much less explored despite suggestions regarding their applicability in bioinspired computation[21,22]. Few experimental demonstrations exist, and only recently has a spiking threshold-driven neurite (the axon of an artificial neuron) been built using a pair of Mott memristors[23].

Here, we introduce an artificial neuron that uses a phase-change device[24] to realize an integrate-and-fire functionality with stochastic dynamics. Using phase-change devices, the actual membrane potential of the artificial neuron can be stored in the form of the phase configuration of a chalcogenide-based phase-change material, which can undergo phase transitions on a nanosecond timescale and down to nanoscale dimensions[25]. We elaborate the concepts of storing and integrating the postsynaptic potentials in phase-change neurons and study both deterministic and stochastic neuronal dynamics. We investigate the computational applicability of phase-change neurons and demonstrate a single-neuron-based computational primitive for detecting temporal correlations in a plurality of event-based data streams. Subsequently, we address the construction of neuronal populations that exploit the stochasticity of individual neurons and enable population-based computations. We focus on representing input stimuli by means of a neuronal population, which is pivotal for population-based computing, and show that an accurate representation is possible even for signals much faster than the firing rate of individual neurons.

Phase-change neurons

An artificial spike-based neuron (Fig. 1) consists of inputs (dendrites), the soma (which comprises the neuronal membrane and the spike-event generation mechanism) and the output (axon). The dendrites may be connected to plastic synapses for interfacing the neuron with other neurons in a network. A key computational element is the neuronal

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