III-V compound semiconductors from van der Waals epitaxy

Researchers have been exploring crystal growth on two-dimensional layered materials such as graphene. Mike Cooke reports.

Although van der Waals (vdW) bonds are weaker than other chemical bonds that are categorized as 'covalent' or 'ionic', large numbers can add up to give effective cohesion in materials in the manner of Velcro. For example, many protein molecules depend on vdW bonds for correct folding of the component polypeptide chains.

Van der Waals epitaxy involves growth on two-dimensional (2D) layered materials such as graphene. In 2D-layered materials there are strong in-plane bonds and weak vdW bonds between the layers. Other 2D layered materials include molybdenum/tungsten sulfide/selenide.

It is hoped that the more relaxed vdW bonding will allow epitaxial (vdWE) growth of 3D crystals on vdW-bonded 2D layers with larger mismatches in lattice constant and thermal expansion. Although the lattice mismatch between graphene and gallium nitride (GaN) is around 23%, a number of research teams have been developing the growth of III-V semiconductor (e.g. GaN) on graphene. However, there are challenges such as suppressed nucleation due to low adsorption and migration energies of adatoms leading to cluster growth rather than single-crystal films.

Bendy blue LEDs on polymer

Much of the research has centered on GaN on graphene. For example, Seoul National University, South Korea, has developed flexible micro-rod light-emitting diodes (LEDs) on polymer using GaN grown on graphene [Kunook Chung et al, APL Mater., vol2, p092512, 2014]. The LED layers consisted of indium gallium nitride (InGaN) multiple quantum wells (MQWs).

Although inorganic compound semiconductor materials have been grown directly on flexible polymer substrates, the thermal budget is very tight. III-nitride semiconductors generally need high temperature for high-quality crystal growth. The Seoul National University used growth on graphene to enable easy release from an inorganic substrate and transfer to polymer as an alternative route to flexible devices.

The graphene was prepared on copper foil by chemical vapor deposition (CVD) and then transferred to silicon dioxide on silicon substrate. The GaN microrods were grown using metal-organic CVD (MOCVD) with trimethyl-gallium (TMGa), ditertiarybutyl-silane (DTBSi) and ammonia (NH_3) precursors in nitrogen carrier gas. Two-step GaN growth at 750–850ºC (3mins) and then 950–1050ºC (30mins) was followed by annealing at 1100ºC (10mins).

The hexagonal micro-rods were grown on a 2μm GaN buffer. The density of rods was $10^7/cm^2$. With the 30 minute growth time, the rods were 1μm in diameter and 7.5μm high. The buffer improved vertical alignment of the rods, allowing fabrication of coaxial quantum wells on the top and sidewalls of the cylindrical rods.

The micro-rods exhibited near-bandedge photoluminescence at 3.4eV photon energy, and at higher pump powers stimulated emission. There was also some weak deep-level emission around 2.2eV. Detailed micro-photoluminescence of a single rod showed no shift in the peak position in spectra from the top, middle and base regions of the rod, suggesting negligible strain fields.

An 8-period quantum well structure of $In_{0.07}Ga_{0.93}N$ in GaN barriers was MOCVD coated coaxially onto the top and sidewalls of the n-type GaN micro-rods. The LED device structure was completed with a coaxial p-GaN layer. The well thickness was estimated at 8nm on the sidewalls and 4nm on the top of the rods. The emission wavelength from cathodoluminescence (electron-beam excited) on the wells was 439nm from the top region and 414nm from the sidewalls, the difference arising from the varying well thickness, according to the researchers.

LEDs were fabricated with metal contact deposition and transfer to polyimide (Figure 1). The rods were insulated from each other by a polyimide fill. Oxygen plasma etch exposed the tips of the rods. The metal contact to the p-GaN consisted of nickel/gold. The

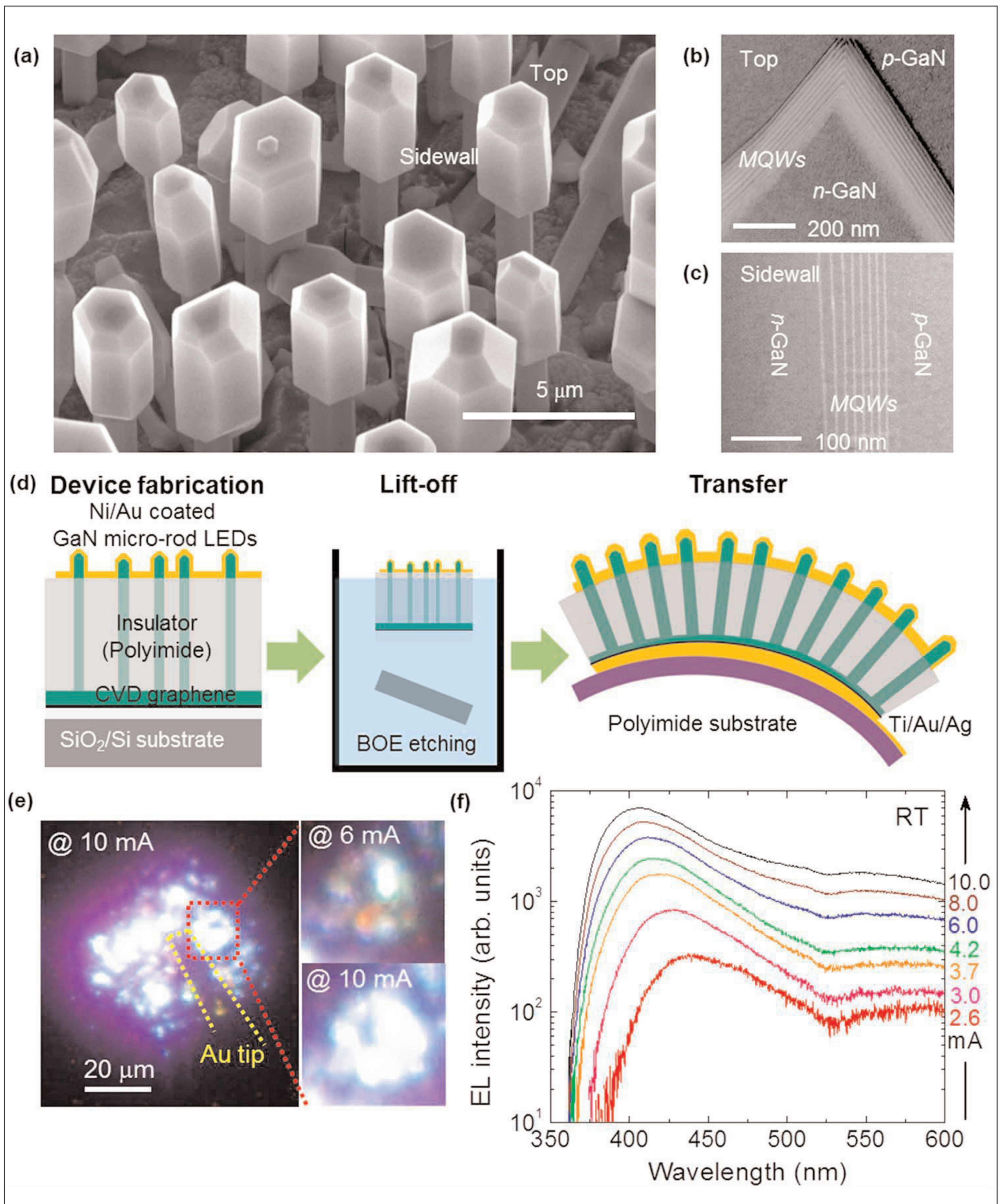

Figure 1. GaN micro-rod LEDs fabricated on graphene. (a) Field emission scanning electron microscope image of coaxial GaN micro-rod LEDs on graphene. Scanning transmission electron microscope images of (b) top and (c) sidewall of MQW layers. (d) Schematic fabrication process for vertical structure micro-rod LEDs. (e) Magnified optical images of LED emission. (f) Power-dependent electroluminescence spectra at room temperature.

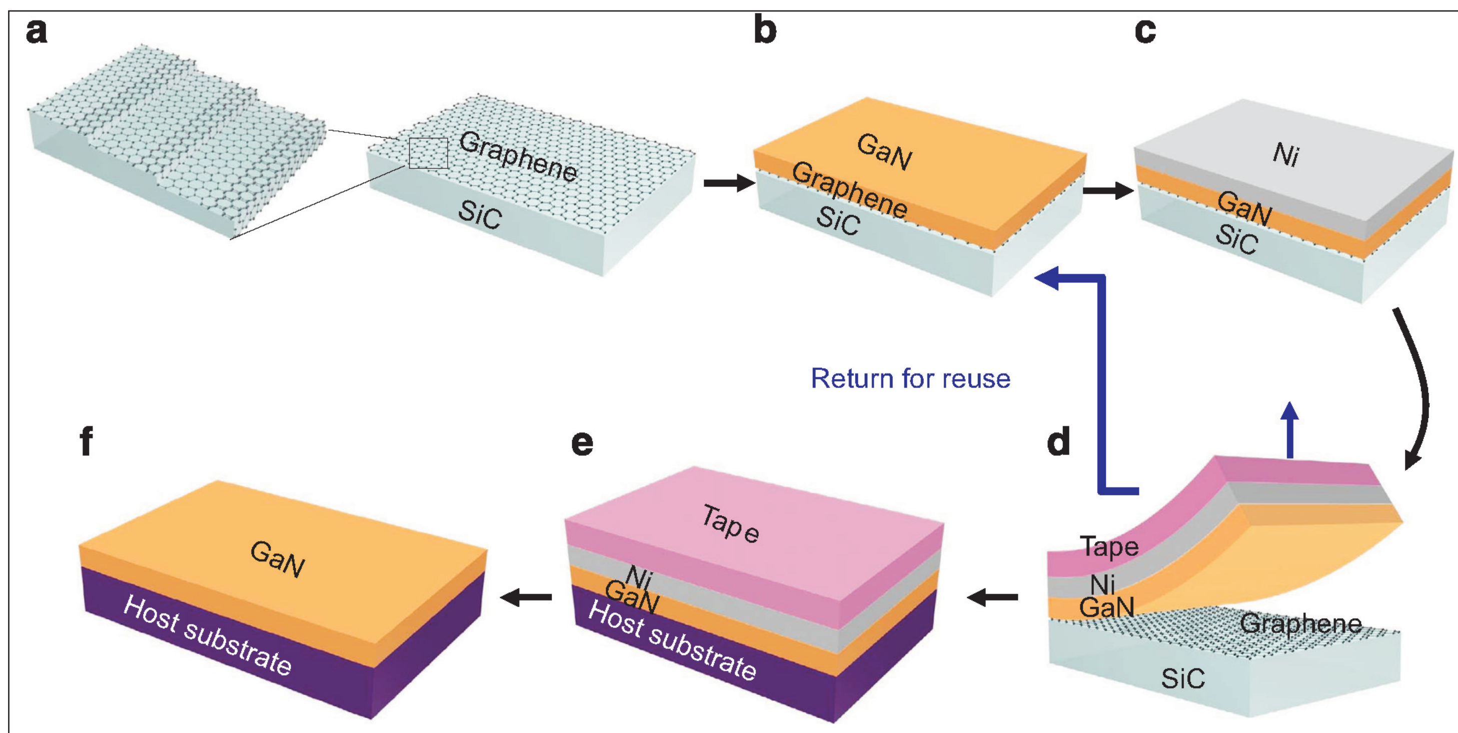

Figure 2. Schematic for growth/transfer of single-crystalline thin films on/from epitaxial graphene. (a) Graphitization of SiC substrate to form epitaxial graphene. (b) Epitaxial growth of GaN on graphene. (c) Deposition of stressor layer (Ni). (d) Release of GaN from substrate with handling tape. (e) Transfer of released GaN/Ni/tape stack to host substrate. (f) Removal of tape and Ni by thermal release and wet etch, leaving GaN film.

n-type titanium/gold contact was made to the base of the GaN buffer, after separation of the epitaxial material from the growth substrate by a wet buffered oxide etch (BOE). An additional thick silver layer was used to give reliable current injection.

The LEDs emitted strong blue light with orange and green from some rods at lower injection (6mA). The longer wavelength emissions turned blue as the current injection increased beyond 10mA. The researchers attribute the orange/green emission to yellow emission in the p-GaN layer. The team believes the yellow emission source could be reduced by optimizing the material growth process.

The devices were also subjected to bending and the electroluminescence suffered no degradation from bending with a 6mm curvature radius. However, bending with a 4mm radius resulted in markedly decreased electroluminescence, suggesting damage from the bending.

GaN and blue LEDs

IBM T. J. Watson Research Center, USA, has also developed vdWE for growth of GaN on graphene. The single-crystal quality of the resulting GaN was comparable to growth on traditional substrates such as sapphire or silicon carbide (SiC) [Jeehwan Kim et al, Nature Communications, vol5, p4836, 2014].

Further, the researchers demonstrated transfer of the crystal material to other materials, allowing re-use of the expensive graphene on SiC growth substrate. The team was able to reuse the substrate and create functioning blue LEDs.

The IBM method starts by forming a graphene layer through graphitizing the surface of the SiC substrate. The graphene growth is self-limiting and results in a layer with vicinal steps that the researchers used as nucleation sites for the subsequent GaN epitaxy (Figure 2). The steps were 5–10nm high and the step terrace width 5–10μm.

A variety of MOCVD processes were tried to create GaN on graphene. The GaN epilayer was limited to ~1cm^2 area due to the small MOCVD reactor used. The researchers found that a modified two-step process at 1100ºC and 1250ºC resulted in continuous and smooth GaN films.

This high-temperature two-step process contrasted with the usual low-temperature/high-temperature process (580ºC/1150ºC) two-step process typically used for deposition on SiC or sapphire. In the case of GaN/graphene growth, the traditional two-step process resulted in GaN clusters. A one-step 1100ºC growth resulted in stripes of GaN on graphene that was attributed to nucleation at the vicinal step edges. A one-step process at 1250ºC resulted in no GaN growth due to the reduced sticking coefficient at higher temperature.

Electron-microscope and diffraction analysis of the GaN film indicated planes of well aligned single-crystalline wurtzite. The researchers estimated the

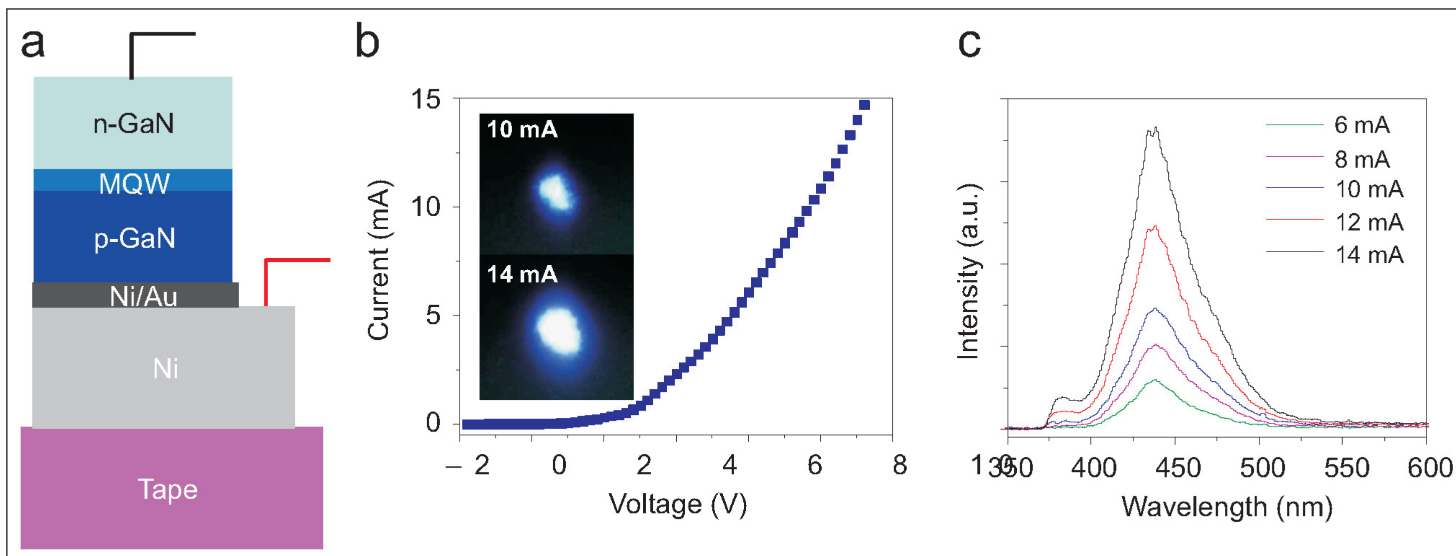

Figure 3. Fabrication of GaN blue LED transferred on tape. (a) Schematic of transferred visible LED device on tape. (b) Current versus voltage (I–V) characteristic of a transferred LED stack. Inset pictures of LED emitting blue light. (c) Electroluminescence (EL) spectra of transferred LED stack.

density of threading dislocations over a 30μm^2 area at around 1x10^9/cm^2. "This density is in the comparable range with that of AlN-buffer-assisted GaN films grown on the conventional substrates, sapphire or SiC by using MOCVD (5x10^8/cm^2–8x10^9/cm^2)," according to the team.

X-ray analysis gave a rocking curve full-width at half maximum (FWHM) value of 0.06º (216arcsec) for the (002) GaN peak. The researchers say this value is similar to that found for GaN on sapphire or SiC.

To release the GaN film, the researchers applied a 2μm nickel layer as stressor to create strain in the 2.5μm GaN film and release the GaN/graphene vdW bonds. Thermal release tape was applied to the nickel for handling and to allow transfer of the GaN layer to another host substrate. The release temperature of the tape was 90ºC.

Atomic force microscopy (AFM) of the GaN surface that was attached to the graphene/SiC showed terrace structures. The researchers believe that this means the entire GaN layer was successfully removed from the growth substrate. Further, Raman spectroscopy could not detect any graphene residue on the released GaN film.

The low surface roughness of 5Å root mean square (RMS) allowed the researchers to directly bond the GaN film to a 90nm silicon dioxide insulator layer on (001) silicon substrate. The researchers comment: "The transferred GaN on insulator shows perfect single-crystalline diffraction patterns indicating no degradation of crystalline quality during the transfer process."

The researchers contrast the low atomic-level surface roughness to the high roughness obtained using laser lift-off substrate separation. In particular, the atomic-scale roughness allows direct bonding without the need for adhesive.

The graphene/SiC substrate was used repeatedly to grow GaN films, confirming the potential for reuse of expensive SiC substrates. Iron chloride (FeCl_3) solution was used to remove nickel residue from the previous release process.

The researchers grew an LED stack on a substrate that had previously been recycled three times. The stack consisted of three 3.5nm indium gallium nitride multiple quantum wells in GaN barriers, along with n- and p-type contact layers.

Nickel/gold was applied to the top p-contact and the structure was released using the nickel stressor/thermal release tape technique. Direct electrical probing showed diode behavior and 40nm wavelength blue electroluminescence (Figure 3).

Gallium arsenide

Researchers have also explored the growth of gallium arsenide (GaAs) on graphene (Figure 4) [Yazeed Alaskar et al, Adv. Funct. Mater., published online 26 August 2014]. The team consisted of personnel from the universities of California at Los Angeles, Riverside and Irvine, and the Saudi Arabia National Nanotechnology Research Center.

The researchers used a Perkin Elmer 430 molecular beam epitaxy (MBE) system to deposit the GaAs on a multilayer graphene buffer on silicon (111) substrate. The graphene consisted of flakes exfoliated using Scotch tape and transferred to the silicon. The surface was cleaned using acetone and isopropanol both before and after the graphene application to avoid and remove traces of organic materials from the exfoliation process.

Raman spectroscopy showed a low response for the disorder-induced D-band peak, which had an intensity

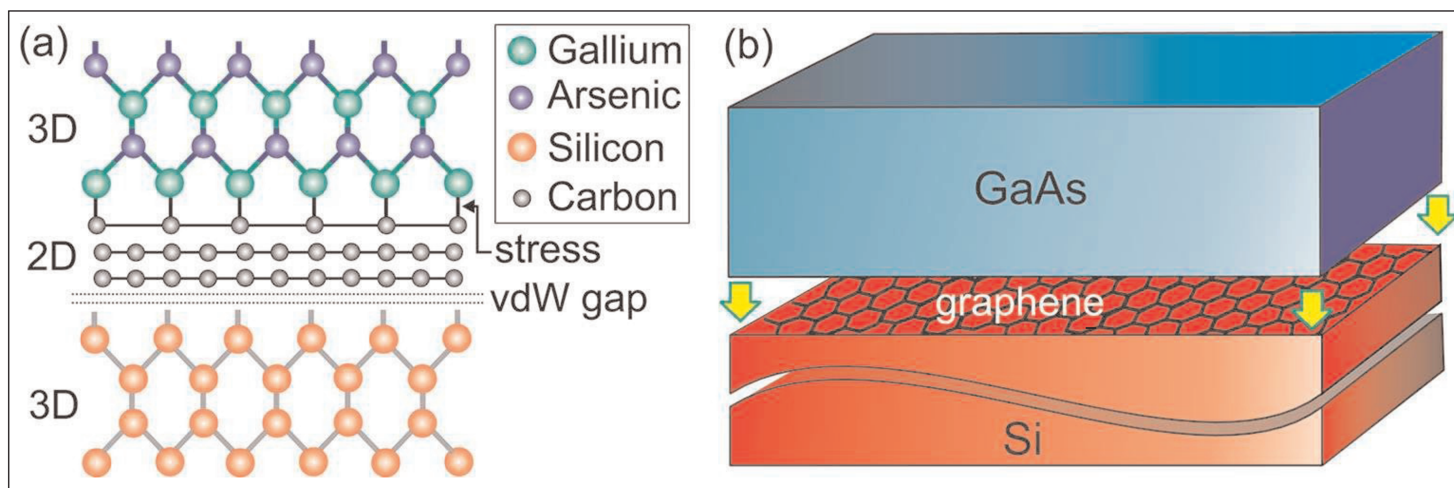

Figure 4. (a) Atomic geometry of GaAs/multi-layer graphene/Si interface showing only topmost graphene layer is strained by heteroepitaxial growth, (b) schematic for structure with GaAs grown on top of single-layer graphene buffer layer/Si substrate.

ratio of less than 0.1 compared with the G-band peak. The Raman result suggests high quality multi-layer graphene. Atomic force microscopy gave a RMS roughness of 0.2nm.

The researchers tried two nucleation techniques. In the first, an arsenic-terminated surface was produced on which GaAs was then grown. In the second, the initial surface termination was changed to gallium.

The As-termination technique resulted in clumping of the GaAs into islands, leading to poor-quality GaAs. For Ga-termination, the research got the best results from two monolayers of Ga. The Ga prelayer was deposited at room temperature. The first deposition of GaAs occurred at 350ºC, avoiding islanding and enhancing nucleation. The surface roughness of the resulting material was found to be as low as 0.6nm RMS.

The researchers comment: "To our knowledge, this result is the first illustration of an ultrasmooth morphology for GaAs films on vdW material."

However, Raman spectroscopy suggested the presence of defects in, and incomplete crystallization of, the nucleation layer. X-ray diffraction rocking curves from the (111) plane had a FWHM of 245arcsec. The researchers say that this suggests that the crystal quality for this orientation requires further improvement.

On the other hand, the FWHM from the 25nm nucleation on graphene is comparable to values achieved in micron-scale GaAs layers grown directly on silicon. "The two-orders-of-magnitude improvement in the quality of our GaAs films can be attributed to the graphene buffer layer mitigating lattice and thermal

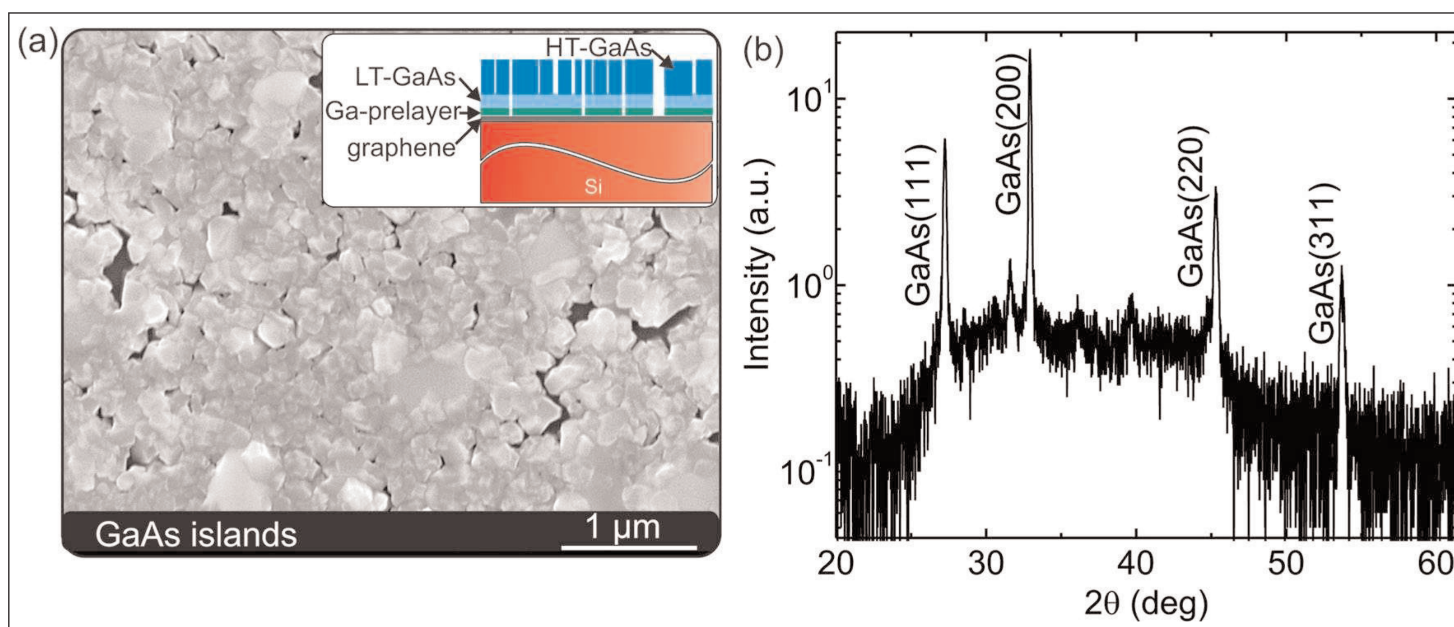

Figure 5. SEM plan-view image of (a) 200 nm high-temperature grown GaAs on top of 25nm thick nucleation layer, with Ga-prelayer and (b) x-ray diffraction scans for GaAs grown by two-step growth, showing polycrystallinity with presence of GaAs (111), (200), (220), and (311).

mismatch between GaAs and the underlying substrate," the researchers write.

Having developed a nucleation layer, the researchers sought to create a two-step process of nucleation followed by raising the temperature to 600ºC to grow a further 200nm of GaAs. This resulted in a polycrystalline film with a faceted surface, due to thermal degradation of the nucleation layer (Figure 5). The researchers attempted to avoid island growth in the high-temperature epitaxy step by increasing the nucleation layer thickness to 100nm, but the problems continued to be apparent. "This suggests the GaAs/graphene interface is not stable at high temperatures," the researchers comment.

Unfortunately, high temperatures are needed to crystallize GaAs and to suppress the effects of defects and dislocations through migration. The researchers suggest through theoretical considerations that the problem resides in low adsorption and migration energies of gallium and arsenic on multi-layer graphene that lead to cluster-growth at high temperature.

Based on their results, the researchers suggest that optimization of the growth parameters in terms of the prelayer or the use of an alternative van der Waals material could lead to single-crystal 2D GaAs on Si. The team is also looking for a low-temperature or modified deposition technique that would eliminate the occurrence of 3D island growth at high growth temperatures. ■

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Mike Cooke is a freelance technology journalist who has worked in the semiconductor and advanced technology sectors since 1997.

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