Exploring graphene applications in nitride semiconductor devices

Researchers are working hard to find commercial uses for graphene in existing and future devices. Mike Cooke reports.

The creation of graphene layers in the past few years has created a landslide of ideas about how the material could be used in a wide range of nanotechnology applications. Although commercial applications where the material is used as the basis for active electronic devices seem some way off, there are possibilities for nearer term employment in auxiliary functions.

One use could be as transparent conducting layers (TCLs) in light-emitting and -absorbing devices. Presently, the material of choice is often indium tin oxide (ITO), which increases in price with indium supply shortages. Also, the transmission of light across ITO TCLs cuts off in the ultraviolet range. The optical transmittance of graphene extends further into the UV than ITO.

TCLs are used to improve current spreading and efficiency of wide-bandgap LEDs, generally for emission in the range from green (~520nm) to deep ultraviolet (~250nm and shorter) wavelengths, based on indium aluminium gallium nitride (InAlGaN) semiconductor alloys.

Much work is being done to apply graphene TCLs in nitride LEDs, but with mixed success. One problem is that the very thinness of graphene leads to reduced conductivity compared with much thicker ITO layers. On the other hand, increasing the number of graphene layers to improve lateral conductivity/current spreading reduces the transmission of light.

An additional problem for graphene TCLs is a large work-function mismatch with the p-GaN that is normally used as the p-contact in nitride semiconductor LEDs. The mismatch results in a high forward voltage needed to drive current through LEDs with graphene TCLs. High forward voltage means power
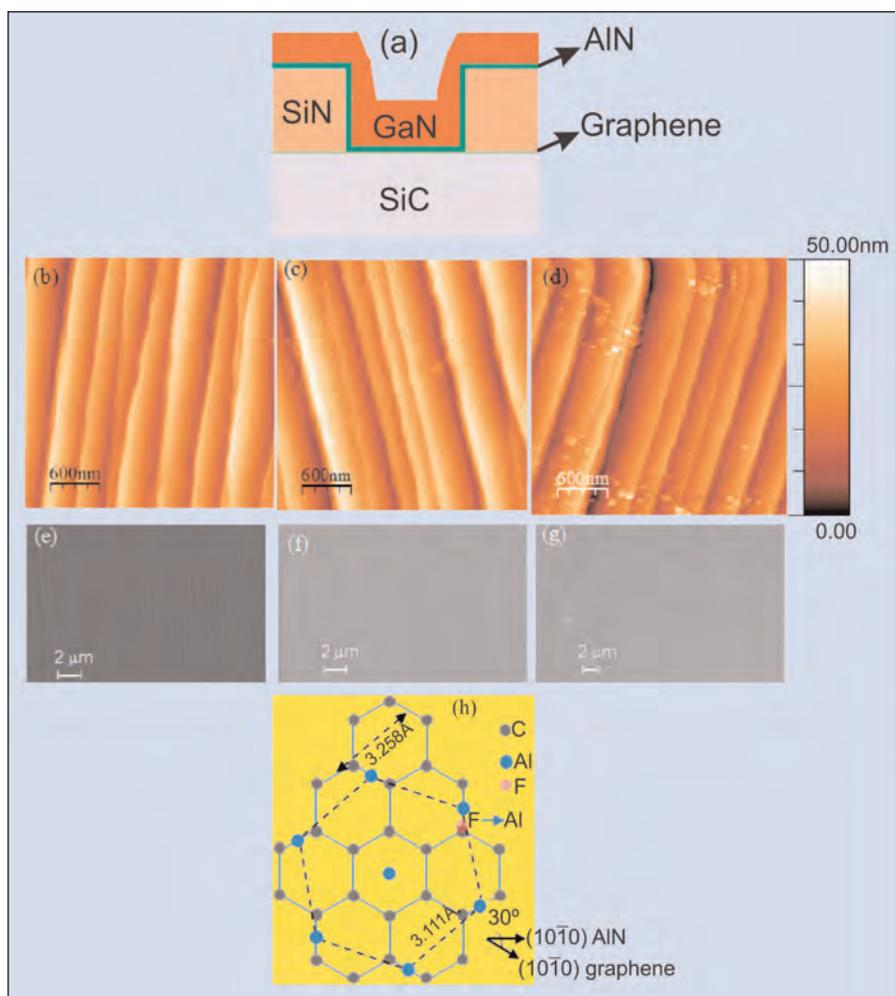

Figure 1 (a) NRL's GaN/AlN/graphene/SiC layered structure. (b) Atomic force microscope (AFM) image of as-synthesized epitaxial graphene, (c) AFM 1.2nm ALE AlN/graphene, (d) AFM GaN/graphene, (e) scanning electron microscope (SEM) image of pristine graphene, (f) SEM 1.2nm ALE AlN/graphene, (g) SEM GaN on AlE AlN/graphene. (h) Al atoms replace F atoms creating AlN nucleation site on graphene resulting in proposed crystalline alignments.

losses and hence lower efficiency.

Here we look at some developments of graphene applied as TCLs in III-nitride LEDs. However, first we discuss a new use of graphene as an underlayer for the growth of nitride semiconductor material.

Looking towards 1THz performance

The US Naval Research Laboratory (NRL) in Washington DC has developed a method to grow epitaxial nitride semiconductors on graphene [Neeraj Nepal et al, Appl. Phys. Express, vol6, p061003, 2013]. The researchers hope that this could lead to high-speed current-switching applications using devices such as hot-electron transistors (HETs).

Existing HETs use heavily doped semiconductor or metal base regions. Heavy doping hampers ballistic transport due to impurity and carrier–carrier scattering effects. Metal base regions suffer from electron reflection effects at the base–collector interface. The NRL team believes that using graphene as the base region, in conjunction with nitride semiconductors, could lead to devices with cut-off frequencies greater than 1THz (1000GHz).

Up to now, the growth of nitride semiconductors on graphene has resulted in non-uniform GaN crystallites and not a continuous film.

The NRL method includes a functionalization step that produces "for the first time" nitride semiconductor layers of a quality similar to that obtained by traditional growth methods on conventional sapphire substrates. In fact, the crystal quality is achieved with thinner layers of less than 1µm compared with layers on other substrates.

The researchers comment: "These results support a successful demonstration of electronic-quality, heteroepitaxial wurtzitic GaN on graphene that is currently unavailable and can improve the performance of present state-of-the-art devices such as HETs."

The initial epitaxial graphene (EG) layer was prepared on 4° off-axis 4H-polytype silicon carbide (1.6mm x 1.6mm squares) using silicon sublimation. Silicon nitride was then applied using plasma-enhanced chemical vapor deposition (PECVD). The silicon nitride was patterned into discs of various diameters between 50µm and 500µm.

The exposed graphene was 'functionalized' by subjecting it to six 30 second pulses of xenon difluoride (XeF_2) plasma. The functionalization consists of creating fluorine-carbon bonds at 6–7% of sites. The bonds are semi-ionic and have been found to preserve the structural and electrical integrity of the graphene, and at the same time to provide nucleation sites for high-quality material deposition.

The nitride semiconductor deposition process must initially ensure that the fluorine atoms are not dislodged, so a low-temperature nucleation is needed. Unfortunately, standard techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) require temperatures of more than 500°C up to around 1300°C.

The NRL nitride deposition began instead with 280°C atomic layer epitaxy (ALE) of 11nm of aluminium
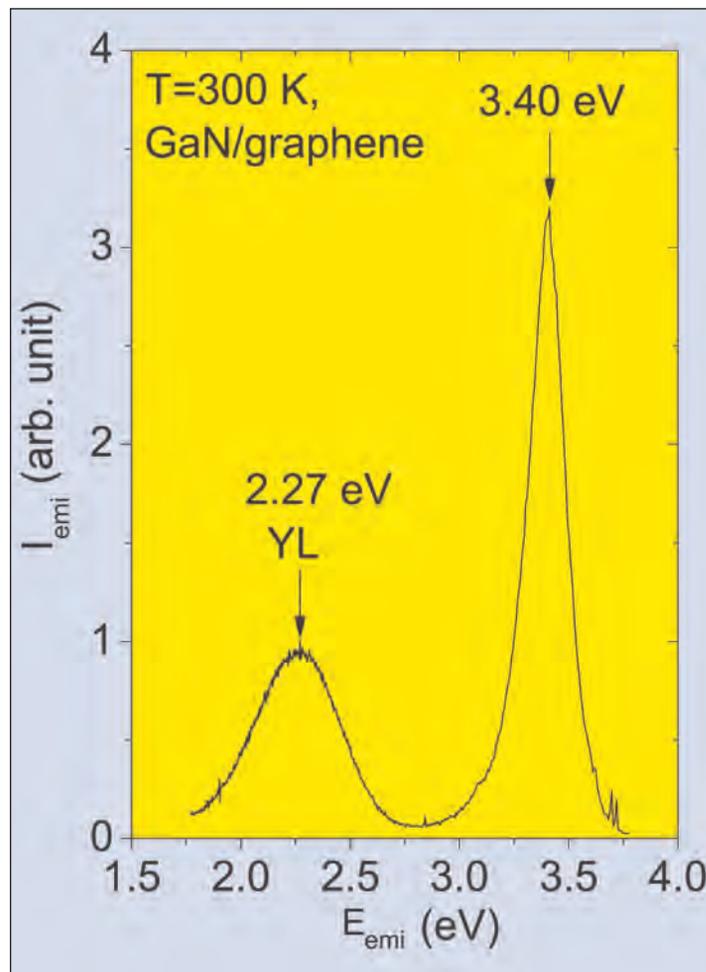

Figure 2. Room-temperature photoluminescence spectra of NRL's GaN on AlN/graphene/SiC stack. Near-band-edge emission is at 3.40eV, broad yellow line at 2.27eV.

nitride (AlN) as a nucleation layer. The lattice mismatch between graphene and AlN is 4.5%, compared with the 13% difference between AlN and sapphire.

The ALE was performed using a 'Fiji' reactor from Cambridge NanoTech. The first five pulses of precursor were of pure trimethyl-aluminium (TMA), designed to promote reaction with the fluorine atoms.

The researchers suggest that the reaction of TMA molecules with the surface fluorine atoms results in a substitution of aluminium for fluorine and the creation of reaction sites for subsequent AlN growth.

Further growth consisted of TMA and nitrogen gas pulses in argon carrier. Unreacted chemicals were purged between pulses with argon. The 11nm AlN layer was grown using 150 cycles. The thickness was determined from an AlN layer grown in the same chamber on a (111) silicon 'witness' substrate. Further growth of 800nm gallium nitride (GaN) semiconductor was performed using MOCVD in a CVD Inc. system.

The material structure (Figure 1) was subjected to a large range of measurements and characterizations during processing. Raman spectroscopy was used to confirm that the growth preserved the graphene underlayer. ▶
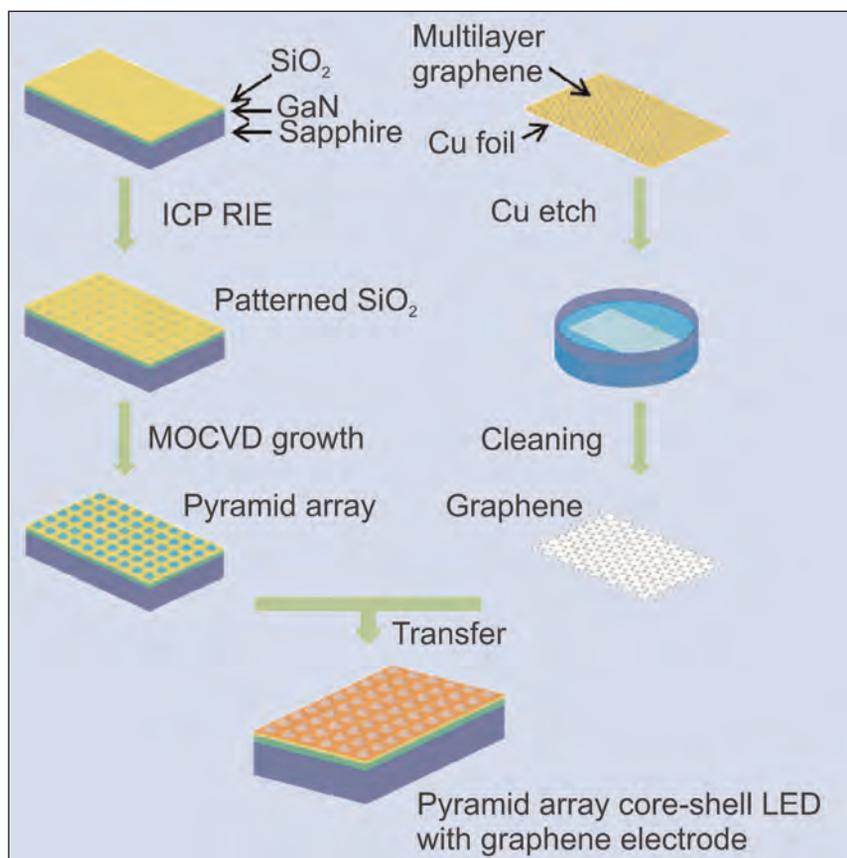
Figure 3. Schematic of key fabrication steps for IOS/Tsinghua pyramid array core-shell LED with graphene electrodes.

► X-ray diffraction studies showed the GaN to have a wurtzite structure, with rocking curve full width at half maximum (FWHM) values of 544 and 461 arcsec for the (0002) and (0004) peaks, respectively. These are similar to those obtained with 5μm GaN on sapphire with a 16% lattice mismatch. "The similarity of these FWHMs for an order of magnitude thinner GaN film may indicate that a better crystalline quality material on EG can be achieved," the researchers comment.

Photoluminescence (PL) spectra show a 3.40eV band edge and a broad yellow line at 2.27eV (Figure 2). The band edge emission could be either due to exciton (electron–hole bound pair) or direct interband recombination. The researchers believe that the yellow line is due to a Ga-vacancy/oxygen complex point defect.

The researchers conclude: "The heteroepitaxial growth of GaN on ALE AlN/EG resulted in a less strained, high-crystalline-quality GaN material under optimized growth conditions. Hence, the optimum properties of both GaN and graphene can be utilized for device applications such as HETs."

Pyramid-array LEDs

Moving on to TCL applications, Chinese Academy of Sciences' Institute of Semiconductors (IOS) and Tsinghua University claim "the first proof-of-concept experimental demonstration of the current-driven pyramid array InGaN/GaN core–shell LEDs intercon-

nected with graphene electrodes". [Junjie Kang, et al, Appl. Phys. Express, vol6, p072102, 2013].

Pyramid array InGaN/GaN core–shell LEDs have been proposed as a way to reduce quantum-confined Stark effects (QCSE) and efficiency droop. Both QCSE and efficiency droop are affected by the presence of electric fields arising from the polar nature of the III-nitride bond. The polar bond gives rise to strain-dependent (piezoelectric) and spontaneous polarization fields.

By combining the pyramid LEDs with graphene transparent conductive electrodes (TCEs) for current spreading and injection, the researchers hoped to demonstrate the use of the latter for non-planar or 3D optoelectronic and photovoltaic devices. The graphene and nitride semiconductor structures were initially processed in two separate branches (Figure 3).

The nitride epitaxy began with MOCVD of silicon-doped n-GaN on c-axis sapphire. This n-GaN template was then prepared for further growth with silicon dioxide used as a photolithographic mask for the growth of the pyramid structures. The mask was prepared with 1μm holes spaced by 1μm.

The light-emitting structures consisted of GaN pyramids grown by MOCVD for 10 minutes, multiple quantum wells (MQWs) of three-pairs of InGaN/GaN on the (1$\bar{1}$01) semi-polar facets of the pyramids, and a 200nm layer of p-GaN. The final pyramid structures were 1.5μm diameter and 1.5μm high. The pyramids had six (1$\bar{1}$01) facets. It has been found that such structures filter out dislocations that can thread up from the template. By growing the MQWs on the semi-polar facets, the polarization field effects leading to QCSE are reduced.

Multilayer graphene was prepared on copper foil by chemical vapor deposition using methane precursor. The graphene was spin-coated with poly(methyl methacrylate) (PMMA) and the copper removed by an iron chloride ($FeCl_3$) solution wet etch. The graphene was then transferred to the nitride semiconductor structure and the PMMA removed in acetone. The graphene transfer process was carried out three times to improve the coverage of the pyramids. Separate measurements on graphene on glass indicated that the transmittance of such multi-layer graphene was around 95% in the visible range.

The LEDs were fabricated using a mesa etch, and application of chromium-platinum-gold contacts. The LED chips measured 177μm x 228μm. In the process graphene was removed selectively using photolithography and oxidation.
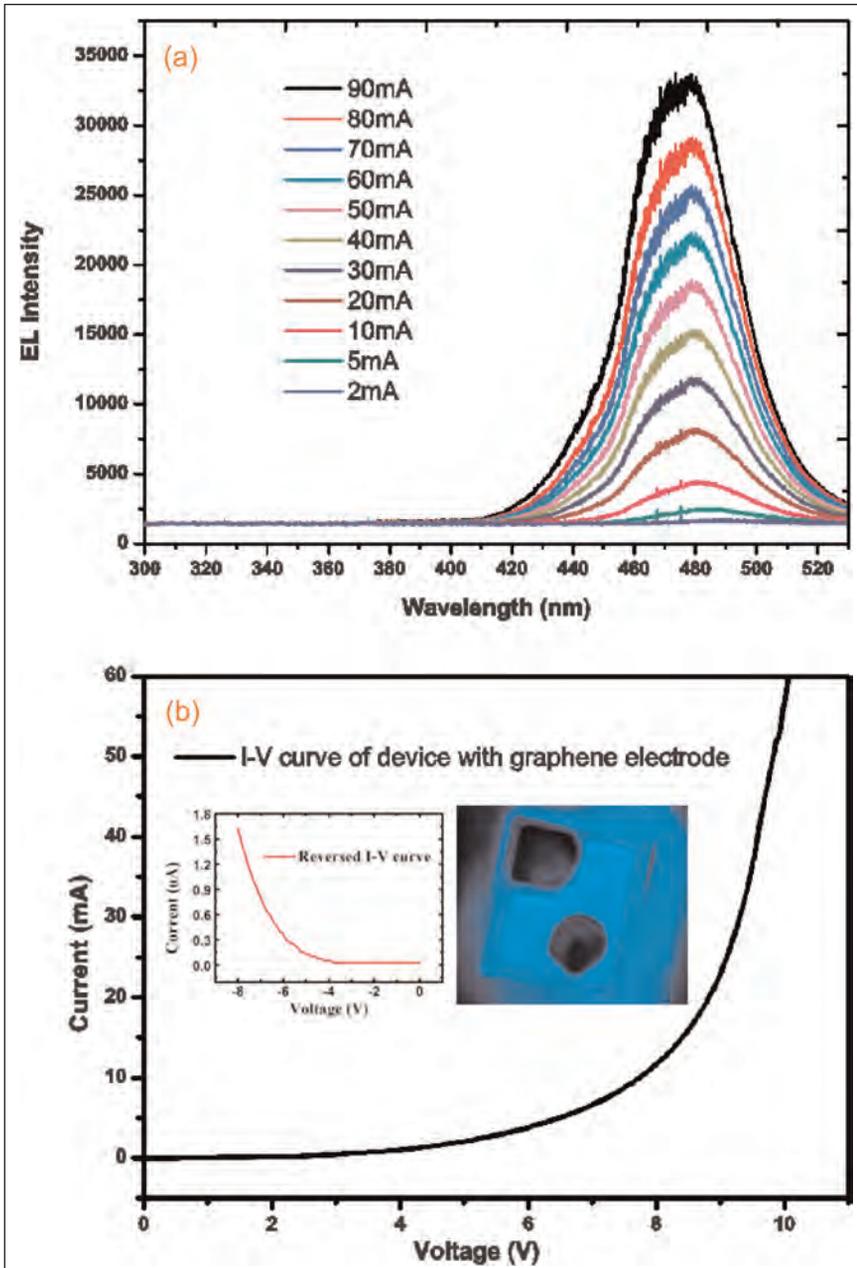
The electroluminescence of the devices peaked around 478nm "with no noticeable spectral shift as the injection current is increased from 2 to 90mA" (Figure 4). This is in contrast to conventional LEDs built from polar c-plane (0001) nitride semiconductors, where QCSEs cause a shift in the peak wavelength.

The width of the emission lines is quite broad, attributed to fluctuation in the indium composition of the MQWs. The current versus voltage behavior shows a reverse current of 1.6µA at –8V. The researchers believe that this indicates that such devices would demonstrate good reliability.

TCL foam

Researchers in Korea have used three-dimensional (3D) graphene foam as transparent conductor for the p-GaN contact of blue LEDs [Byung-Jae Kim et al, Appl. Phys. Lett., vol102, p161902, 2013]. The team consisted of engineers from Korea University, Sunchon National University, and Hongik University.

The effect of using graphene foam was to reduce the forward voltage by 26% and to increase light output by 14%. Both factors

Figure 4. (a) Room-temperature electroluminescence spectra of IOS/Tsinghua pyramid array core-shell LEDs at various current injections. (b) Current versus voltage (I–V) curve of LEDs with multilayer graphene electrode. Inset: photograph of light emission from single LED chip and reversed bias current–voltage curve.
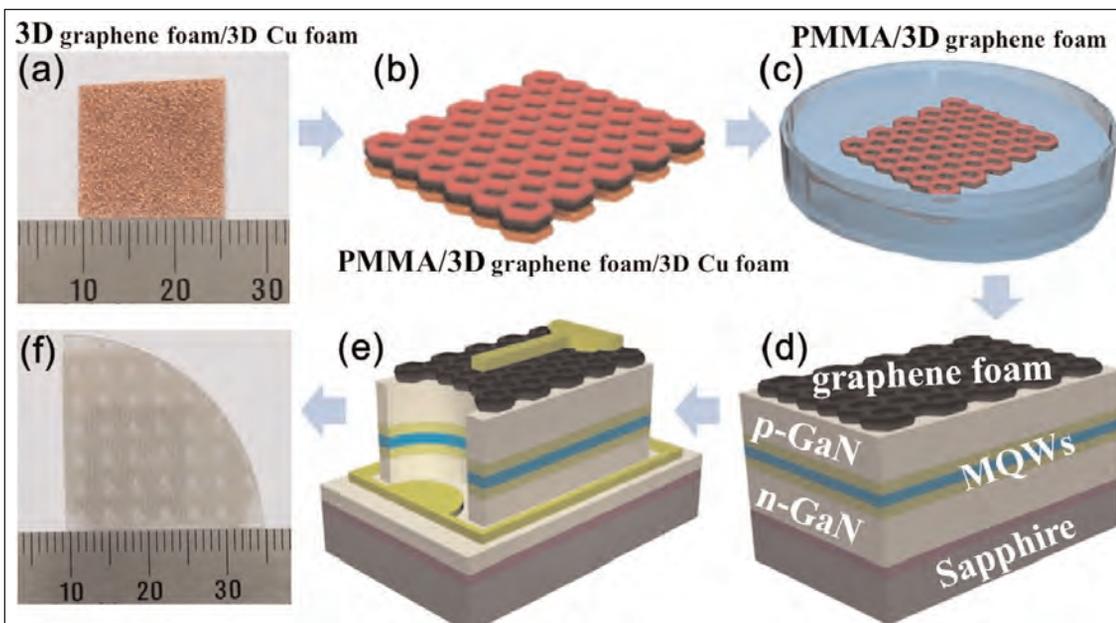

Figure 5. Korea University etal's fabrication of blue LEDs with 3D graphene foam-based TCEs: (a) 3D graphene foam grown on 3D Cu foam; (b) spin-coating with PMMA; (c) wet etch of copper; (d) transfer of 3D graphene foam to p-GaN layer of blue LED material and removal of PMMA; (e) and (f) blue LED devices fabricated with standard processes.
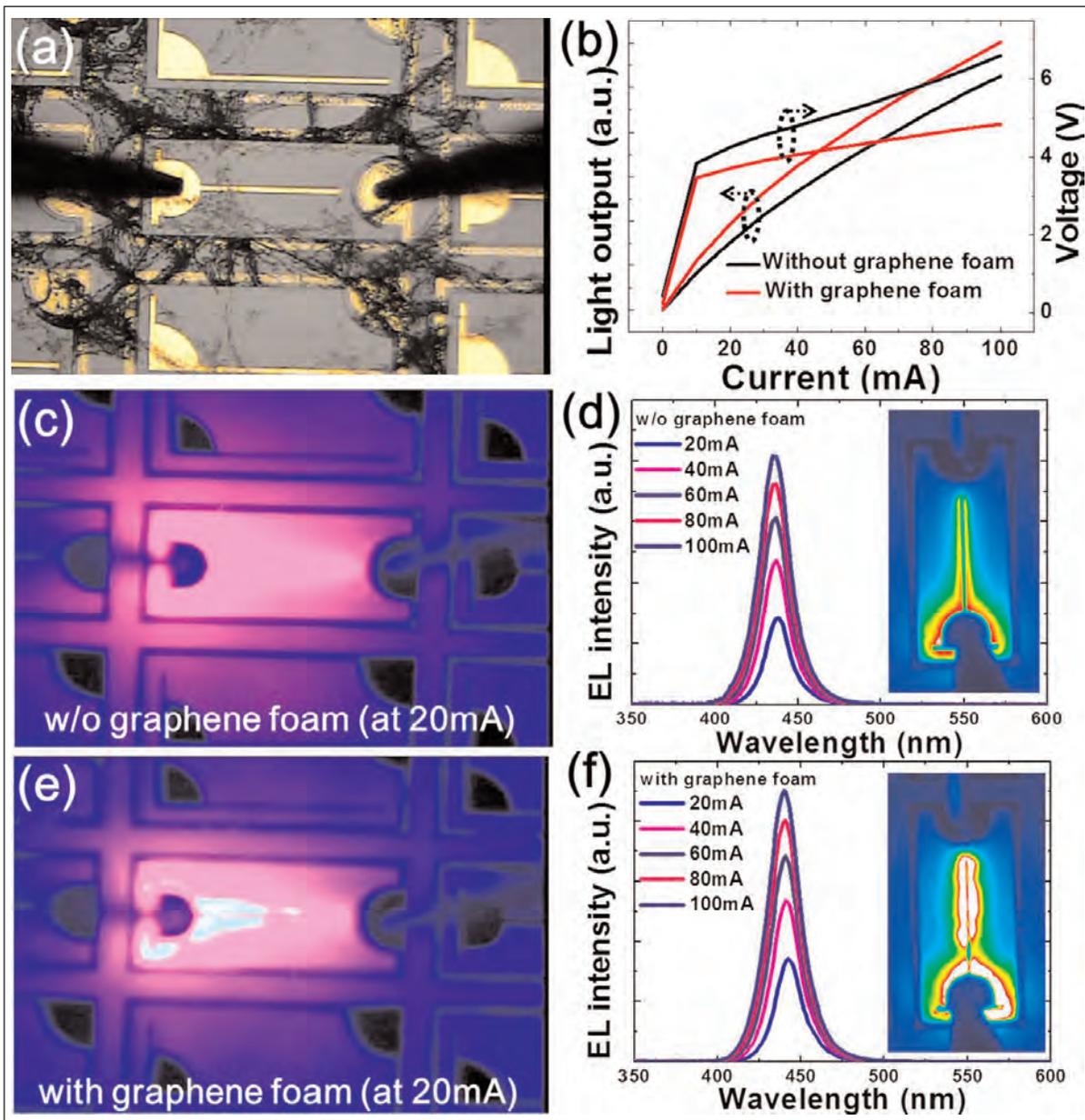
Figure 6. (a) Korea University et al's optical microscope image of blue LED devices with graphene foam TCE. (b) Light output and current versus voltage (L–I–V) characteristics of blue LEDs with/without graphene foam. (c) Electroluminescence (EL) image of blue LED device without graphene foam at 20mA. (d) EL spectra of blue LED without graphene foam in 20–100mA range. (e) EL image of blue LED with graphene foam at 20mA. (f) EL spectra of blue LED with graphene foam in 20-100mA range. Insets of (d) and (f) are optical light emission images from beam profiler without/with graphene foam.

foam on nitride semiconductor structure was fabricated into LED devices with plasma-etched mesas, titanium/aluminium/nickel/gold contacts with the n-GaN layer, and titanium/gold n- and p-contact pads.

Graphene foam suffers from reduced transmittance compared with bilayer graphene. At 438nm wavelength, the transmittance of foam is 71%, while that of a bilayer is 95%. However, the foam is closer to 150nm ITO's 75% transmittance at the same wavelength. The researchers point out that foam does have advantages over bilayer graphene such as low mass density, large surface area, high thermal and electrical conductivity, and good mechanical stability. The foam has a sheet resistance of ~800Ω/square, compared with 1500–3000Ω/square for 2D graphene films.

suggest improved power efficiency. Before this research, graphene foam had not previously been applied to light-emitting or -absorbing devices (e.g. solar cells).

Commercial 3D graphene foam was used, produced on 3D copper foam using chemical vapor deposition. The material was spin-coated with PMMA and the copper etched away in ammonium sulfate $((NH_4)_2S_2O_8)$ solution (Figure 5). The graphene foam was cut into a square and transferred to the p-GaN layer of a commercial blue LED nitride semiconductor epitaxial material on sapphire substrate. The assembly of graphene

The LED chips measured 200μm x 500μm. At 100mA current injection, the forward voltage was 4.85V while without the foam the value was increased to 6.61V (Figure 6). Also, light output increased 14% at 100mA from the better current-spreading capability of the foam.

The researchers comment that the fabrication process of graphene foam needs to be optimized. For example, the foam structure partially collapsed during the photolithography processing that involves spin-coating
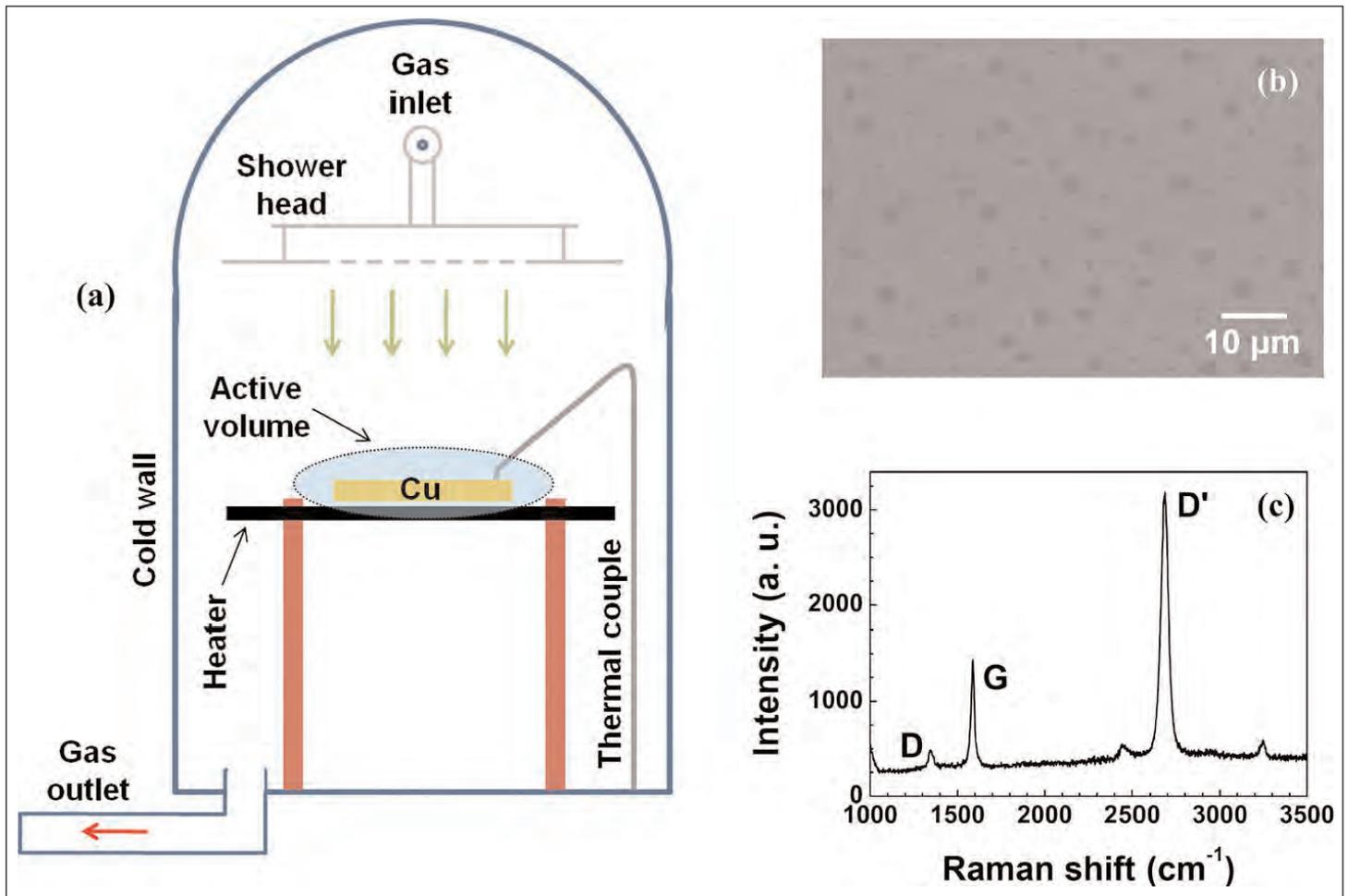
Figure 7. (a) Schematic of cold-wall CVD used by Beijing/Chalmers. Gases are injected from shower head over sample on heater. Active hot volume is very small compared with hot wall systems. (b) SEM image of high density graphene nucleation during early stage deposition on liquid Cu, captured after cooling to room temperature. (c) Typical Raman spectrum of graphene. D' peak is more than twice G peak. Small D peak indicates high quality of film.

of the photoresist, development, plasma etch, and lift-off steps. Some photolithography residue was seen in electron and optical micrograph images as structures with a spider-web appearance. Raman spectroscopy confirmed that the web-like material was not graphene.

Fast-growth graphene

Researchers based in China and Sweden have proposed fast graphene CVD as a route to more cost-effective TCLs for nitride LEDs [Xu Kun et al, Appl. Phys. Lett., vol102, p162102, 2013]. The research involved China's Key Laboratory of Optoelectronics Technology (Beijing University of Technology) and Sweden's Chalmers Tekniska Högskola AB.

While the fabrication of high-quality single-crystal graphene can take many hours, the proposed poly-crystalline graphene is grown in half an hour. Despite its polycrystalline nature, the resulting graphene is found to have conductivity similar to that of normal graphene prepared by more laborious methods.

The fast graphene was grown on polycrystalline

copper foil in a cold-wall Aixtron CVD system (Figure 7). The substrate was first cleaned, then heated to 1000°C at 300°C/min and annealed for 5 minutes. The graphene source was methane (CH_4) in hydrogen/argon. The growth step was only 5 minutes. The sample was quench-cooled by shutting off the heater. The researchers see the fast growth rate as being related to the small active region with a high concentration of reactants near the deposition site enabled by the use of a cold-wall system.

The epitaxial structure for the LED (Figure 8) was a commercial product grown on c-plane sapphire. The material was fabricated into mesa-structure LEDs with different TCL structures. ITO layers were produced using electron-beam evaporation. The graphene was transferred to the ITO surface by spin coating a PMMA mechanical support layer and etching away the copper foil in ferric chloride ($FeCl_3$) solution.

The mesa structures were defined by photolithography and plasma etching of graphene, ITO and nitride semiconductor. The metal electrodes consisted of titanium/gold.
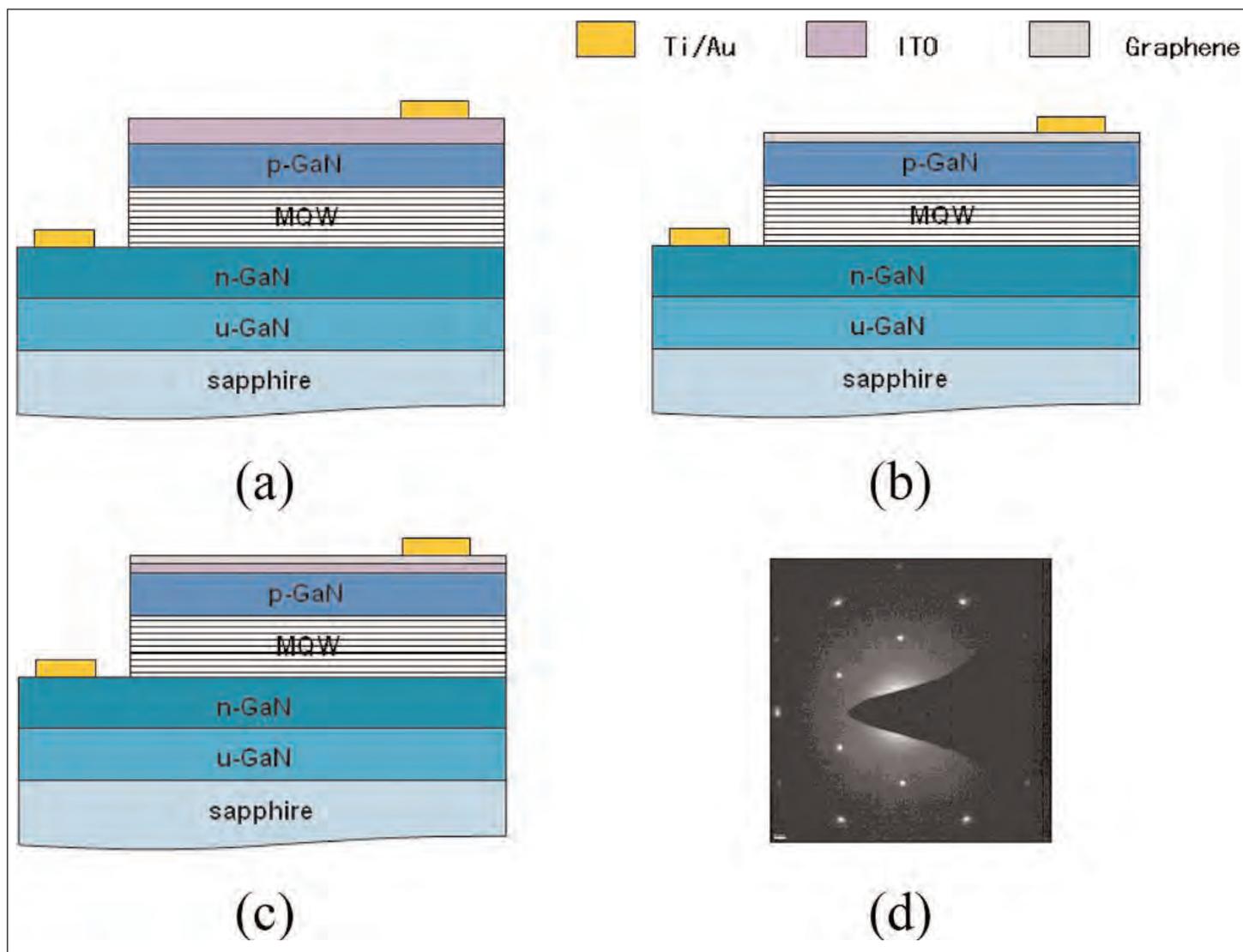
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Figure 8. Beijing/Chalmers LED structures with various TCLs: (a) type I (240nm ITO), (b) type II (3-layer graphene), and (c) types III, IV, and V (3, 7, and 10 nm ITO+3-layer graphene). MQW denotes multiple quantum wells. (d) Typical selected area electron diffraction pattern of graphene. Six-fold symmetric dots with equal intensity strength indicate high quality monolayer graphene.

Monolayer graphene as-deposited had a sheet resistance range of 800–1000Ω/square. Increasing the number of layers to three reduced the range to 300–350Ω/square. The mobility was around 2000cm^2/V-s. The sheet resistance values are similar to those achieved for standard graphene.

Optical inspection of the light emission at 20mA showed that the devices with graphene emit more uniformly across the device, indicating successful current spreading. By contrast, a 10nm ITO-only TCL LED emitted more brightly closer to the p-electrode.

The work-function mismatch between graphene and p-GaN resulted in a high 6.76V forward voltage needed to drive 20mA current through a 3-layer graphene device. By inserting a thin 7nm ITO layer the forward voltage was reduced to 3.90V. An LED with 240nm ITO layer had a forward voltage at 20mA of 3.6V.

An alternative technique to bring the graphene work-function closer to that of p-GaN is doping. However, the known techniques for this are not stable over time. Another way forward may be to grow carbon films directly on p-GaN. Adhesion of graphene is generally better to GaN than GaAs, due to a closer lattice affinity. Researchers at Chalmers recently reported a technique for direct growth on p-GaN that resulted in a carbon film with "optical transparencies comparable to that of exfoliated graphene" [Jie Sun et al, IEEE Transactions on Semiconductor Manufacturing, vol25, p494, 2012].

In terms of optical transmission, although the 10nm ITO+3-layer graphene and 240nm ITO TCLs perform comparably at long wavelengths, at ultraviolet wavelengths of 320nm the former transmits 78.6% and the latter 58.9%. ∎

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