Transferring graphene to nitride optoelectronics

Researchers are keen to find practical applications for graphene. In the past year or so, scientists and engineers have been looking at the material's possible use in combination with nitride semiconductor optoelectronic devices such as LEDs and solar cells. Mike Cooke reports recent developments.

Graphene electrodes have recently been proposed as transparent conducting layers (TCLs) for spreading current uniformly across shorter-wavelength (blue-ultraviolet) nitride semiconductor light-emitting diodes (LEDs) and solar cells (SCs). In nitride light-emitting and absorbing devices, current spreading is essential in producing more efficient devices at high output power.

The hopes of those who are developing graphene as a TCL is to create current-spreading electrodes with high transparency, conductivity and flexibility at low cost for volume manufacturing. Other transparent conducting materials such as indium tin oxide (ITO) begin to cut off in the UV region. Also, indium is an expensive material. However, while graphene has better transparency characteristics, apart from being more experimental, its electrical conductivity tends to be lower because of the thinness of the layer.

200nm	p-GaN	Cladding/contact
	InGaN/GaN	Quantum wells/barriers
2µm	n-GaN	Cladding/contact
2µm	u-GaN	Buffer
	Sapphire	Substrate

Figure 1. Epitaxial structure of nitride semiconductor LED / SC material. The buffer and n-contact were grown at 1020°C; the multi-quantum wells at 800°C; and the p-contact at 980°C.

Previous reports in Semiconductor Today have centered on the possibility of use as TCL for UV-LEDs (Mike Cooke, Semiconductor Today October/November 2011, p104), showing improved light output over devices with ITO TCL (www.semiconductor-today.com/news_items/2011/DEC/SEO_311211.html) and using a graphene/zinc oxide nanorod composite to increase light output and to improve current injection (www.semiconductor-today.com/news_items/2012/ FEB/HANYANG_290212.html).

Gold nanoparticle boost

Researchers in Korea have been studying how to improve graphene transparent conducting layers (TCLs) using gold nanoparticle (Au-NP) decoration [Minhyeok Choe et al, Appl. Phys. Lett., vol101, p031115, 2012]. The team was variously associated with Gwangju Institute of Science and Technology, Korea Basic Science Institute Jeonju Center, and Seoul National University.

The aim of applying the Au NPs was to control the graphene work function and conductivity performance. Work function matching is important in creating high injection currents in LEDs (and hence high output) and low series resistance in SCs (boosting conversion efficiency).

The graphene was formed in a chemical vapor deposition process on 300nm-thick polycrystalline nickel on silicon dioxide/silicon (SiO_2/Si). The methane source gas was delivered in a hydrogen/argon gas mix. The substrate temperature was 900ºC. The multi-layer graphene (MLG) layer was released from the nickel by a wet etch in iron chloride ($FeCl_3$) solution. The Au-NP decoration was achieved through immersion in gold chloride ($AuCl_3$) solution.

The graphene was transferred to nitride semiconductor LEDs and SC epitaxial structures (Figure1) grown using metal-organic chemical vapor deposition on sapphire. The n-contact regions were exposed by etching with inductively coupled plasma through the p-type gallium nitride (GaN) and indium gallium nitride (InGaN) multi-quantum well (MQW) layers. The MLG was transferred onto the p-GaN. The MLG over the n-contact regions was removed with photolithographic patterning and reactive-ion etch. The n-contact electrode consisted of chromium/gold. The MLG formed a transparent conducting electrode for the p-contact.

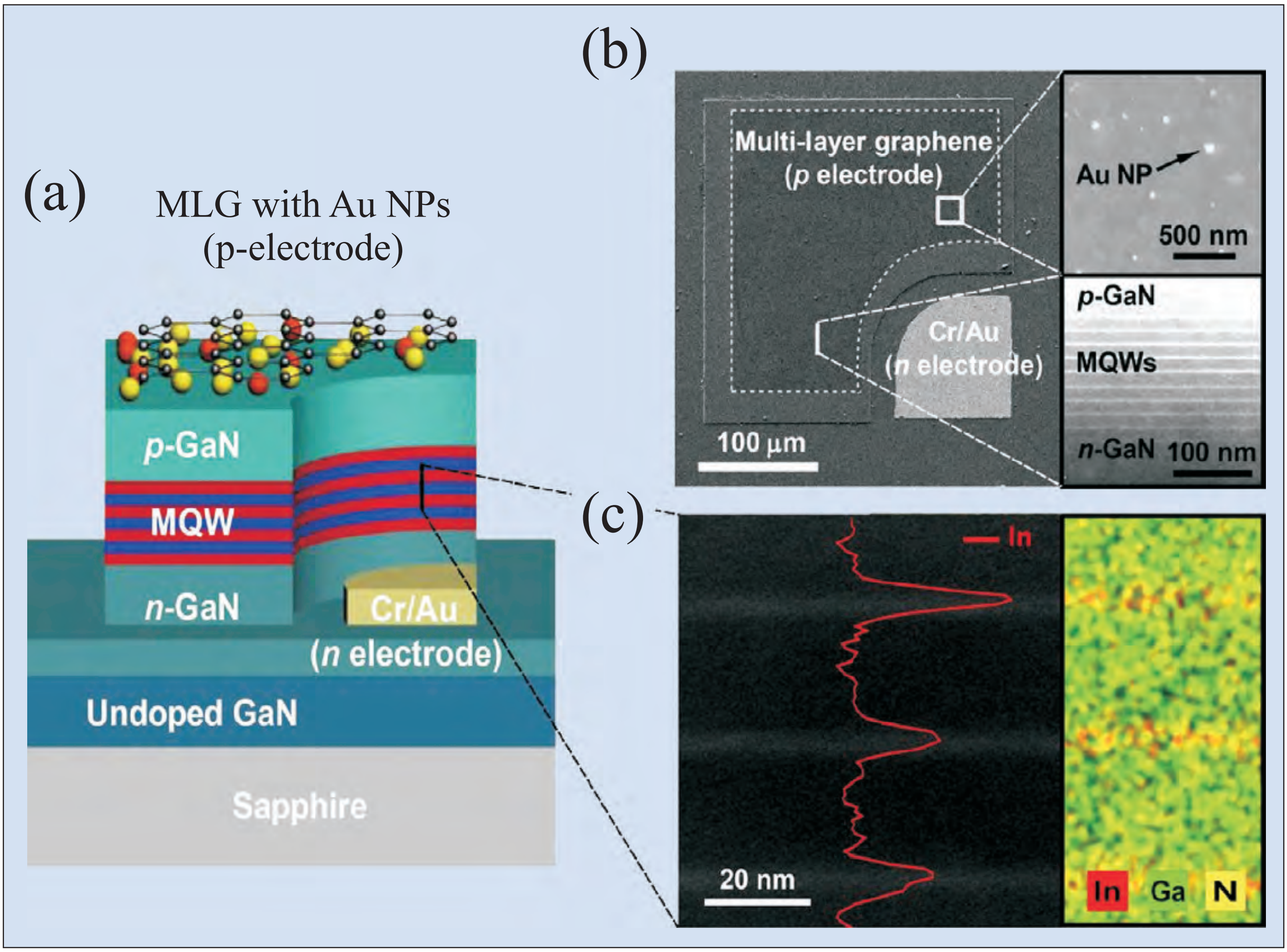

Figure 2. (a) Schematic illustration of MLG-electrode GaN-based LED device. (b) Plan-view SEM image of GaN-based LED device. Insets show SEM image of MLG with Au NPs (top) and TEM image of MQWs (bottom). (c) Magnified TEM image and energy-dispersive x-ray (EDX) mapping of the MQWs.

Various measurements (UV photoelectron and Raman spectroscopy) on MLGs with Au-NPs suggest a hole-doping effect and an increase in work function. One negative effect of adding Au-NPs is to reduce transmittance of near-UV 400nm wavelength light: the transmittance was 89% for MLG without Au-NPs, but 85% for MLG with Au-NPs deposited from a 5mMol/litre (5mM) $AuCl_3$ solution. Increasing the NP density with a 20mM solution further cut transmittance to 78%.

Hall measurements showed a reduction in sheet resistance and an increase in hole density from applying Au-NPs. The sheet resistance without Au-NPs was ~1000Ω/square, falling to ~200Ω/square and ~100Ω/square for the 5mM and 20mM Au-NP treatments, respectively. The respective hole densities were ~10^{13}/cm^3 (no Au-NPs), ~10^{14}/cm^3 (5mM), and ~2x10^{14}/cm^3 (20mM).

Further transmission electron microscope examination of samples gave the estimated thickness of the MLG as about nine layers with an interlayer distance of ~4Å.

When the MLG structures were applied as TCL to nitride semiconductor LEDs (Figure 2), the addition of Au-NPs reduced the forward voltage at 0.4mA to 3.94V (5mM) and 3.86V (20mM) from 4.73V for the TCL without Au-NPs. The reduced forward voltage with Au-NPs is attributed to the smaller work function difference between TCL and p-GaN allowing high current injection into the MQWs. However, the injection at present is not as good as that obtained with ITO TCLs.

Electroluminescence (EL) spectra (Figure 3) indicate that the peak wavelength did not shift noticeably with higher current. The best light output performance at 500µA was obtained from 5mM Au-NPs with 94% better performance than without NPs and 29% better performance than the TCL with 20mM Au-NP treatment. The worse light emission performance from the 20mM device is attributed to the reduction in transmittance.

The researchers comment: "By optimizing the concentration of the Au NPs for electrical conductivity and transparency, the current injection and light emission efficiency of the MLG-electrode GaN-based LEDs may be further enhanced."

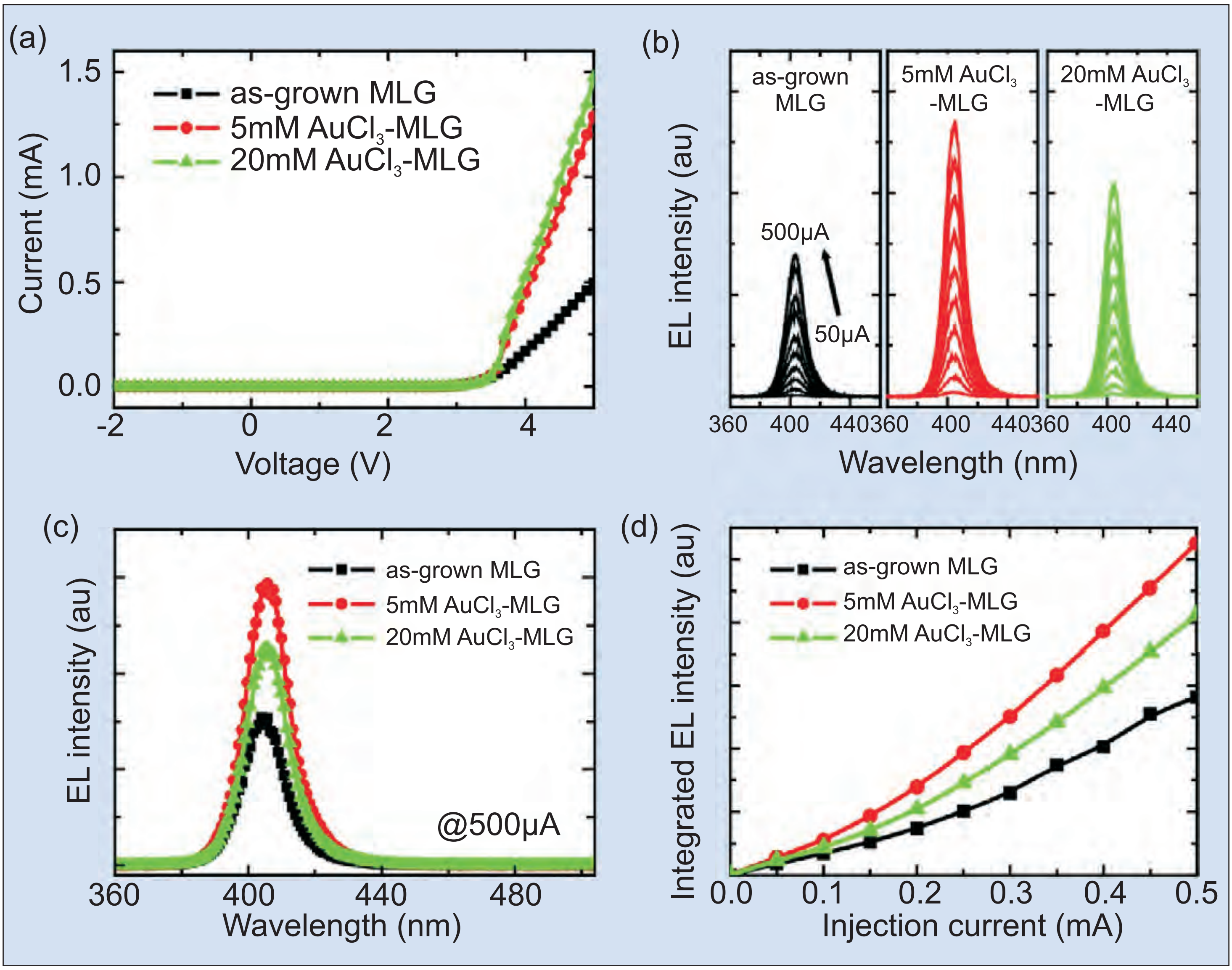

Figure 3. (a) Current–voltage (I-V) curves of GaN-based LEDs with as-grown MLG, 5mM $AuCl_3$-MLG, and 20mM $AuCl_3$-MLG. (b) EL intensity of the MLG-electrode GaN-based LEDs as a function of injection current. (c) EL intensity of MLG-electrode GaN-based LEDs measured at 500μA. (d) Integrated EL intensity of MLG-electrode GaN-based LEDs as a function of injection current.

For SCs (constructed in same way as the LEDs), the best performance was obtained from 20mM Au-NP MLG. For AM1.5G solar illumination, the short-circuit current was 0.67mA/cm^2, the open-circuit voltage 2.25V, and the fill factor 0.77, giving a power conversion efficiency of 1.2%.

The low level of power conversion is due to the peak response being around 400nm (UV), while the bulk of solar radiation is in the infrared-to-green regions (wavelengths longer than 500nm). However, such devices could be used as part of a multi-junction system to extract energy from short-wavelength sunlight. Further, it is hoped in future to create suitable high-quality InGaN quantum wells with narrower bandgaps that respond to longer wavelengths.

The power conversion for SCs that include MLG electrodes without Au-NPs was around 0.9% (short-circuit current 0.51mA/cm^2). The improved performance for 20mM Au-NPs is attributed to improved conductivity (boosting currents), better light absorption, and to a lower energy offset between the TCL and p-GaN (slightly increasing the open-circuit voltage).

Silicon nitride protection

Korea University, US Naval Research Laboratory and University of Florida have improved the reliability of graphene electrodes in ultraviolet light-emitting diodes (UV-LEDs) through application of 20nm silicon nitride (SiN) to avoid oxidation of the material at high temperature [Byung-Jae Kim et al, Appl. Phys. Lett., vol101, p031108, 2012].

The epitaxial material for the UV-LEDs (Figure 4) was grown on sapphire using metal-organic chemical vapor deposition. The few-layer graphene (FLG) was grown at 1000ºC on copper foil using methane as the carbon source for the graphene and hydrogen as the carrier. The graphene was covered with poly(methyl methacrylate) (PMMA) to allow etching away of the copper in sulfuric acid solution for 6 hours. The graphene was then transferred onto the epitaxial material before standard processing into mesa-type LEDs with metal electrodes.

When subjected to 10V bias for 30 seconds, these devices suffered serious degradation in performance both in terms of light emission and electrically (Figure 5). Before biasing, the LEDs showed bright emission from across the chip, but afterwards light came only from near the metal electrodes. The current–voltage curves also showed reduced current from the device stressing.

A pulsed bias condition (5% duty cycle) of 10V for 30 seconds was also applied to fresh devices to remove self-heating effects. Although the effect was not as severe, partial degradation of the performance was also seen.

The degradation was attributed to oxidation reducing the thickness of the FLG layer. It was estimated that, before the continuous bias, the FLG consisted of four layers, reducing to two layers after the electrical/thermal stress. The oxidation is thought to occur more readily at edges and defect sites. In the continuous bias test, the reduction in light emission proceeded from the outer edges of the graphene.

To avoid these effects, the researchers applied 20nm silicon nitride to the devices using a Unaxis plasma-enhanced chemical vapor deposition (PECVD) system. The aim was to protect the FLG from attack by oxygen. Silicon nitride has an intermediate refractive index of ~2.1, between the values for GaN (~2.5) and air (1). Also, SiN has high transmittance of UV light.

The SiN-passivated LEDs suffered much less degradation under 10V continuous bias (Figure 6). Further, the time for current to fall to half the initial value was 3–6 minutes.

200nm	GaN:Mg	p-cladding
8nm	AlGaN	Barrier
5nm	GaN	Single quantum well
8nm	AlGaN	Barrier
2µm	GaN:Si	n-cladding
25nm	AlN	
	Sapphire	Substrate

Figure 4. Epitaxial material for UV-LEDs. AlN deposited at 680°C, 50Torr; other layers at 1025°C,

The researchers comment: "Since this SiN_x-based passivation technique is compatible with current manufacturing process, it will be convenient and effective for improving the reliability of the graphene-based electronic/optoelectronic devices."

Vertical InGaN LEDs application

Researchers in China have applied graphene as transparent conducting layers (TCL) in vertical light-emitting diodes (VLEDs) made from indium gallium nitride (InGaN) semiconductors [Liancheng Wang et al, Appl. Phys. Lett., vol101, p061102, 2012]. The researchers were based in Beijing at Chinese Academy of Sciences'

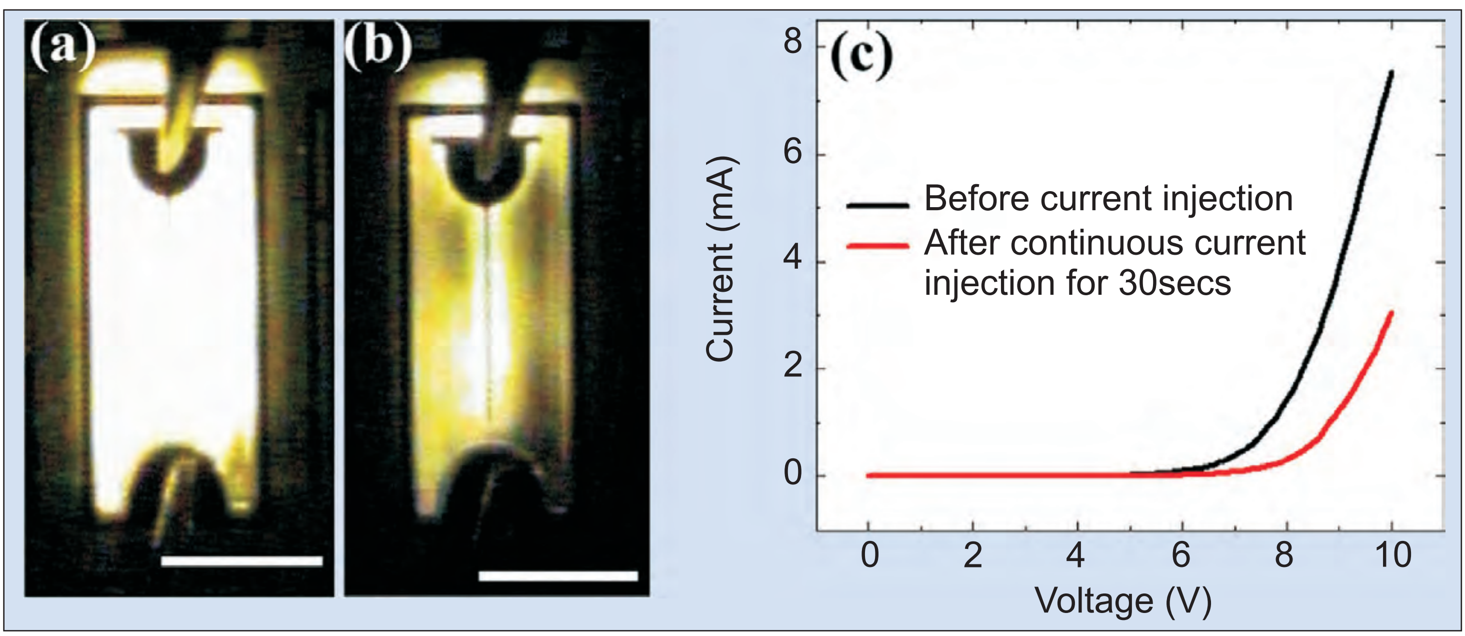

Figure 5. Microscopic electroluminescence images of UV-LED without SiN_x layer (a) before (b) after applying continuous current injection for 30s at forward bias of 10 V. (c) Current vs voltage (I–V) characteristics from UV-LED without SiN_x layer.

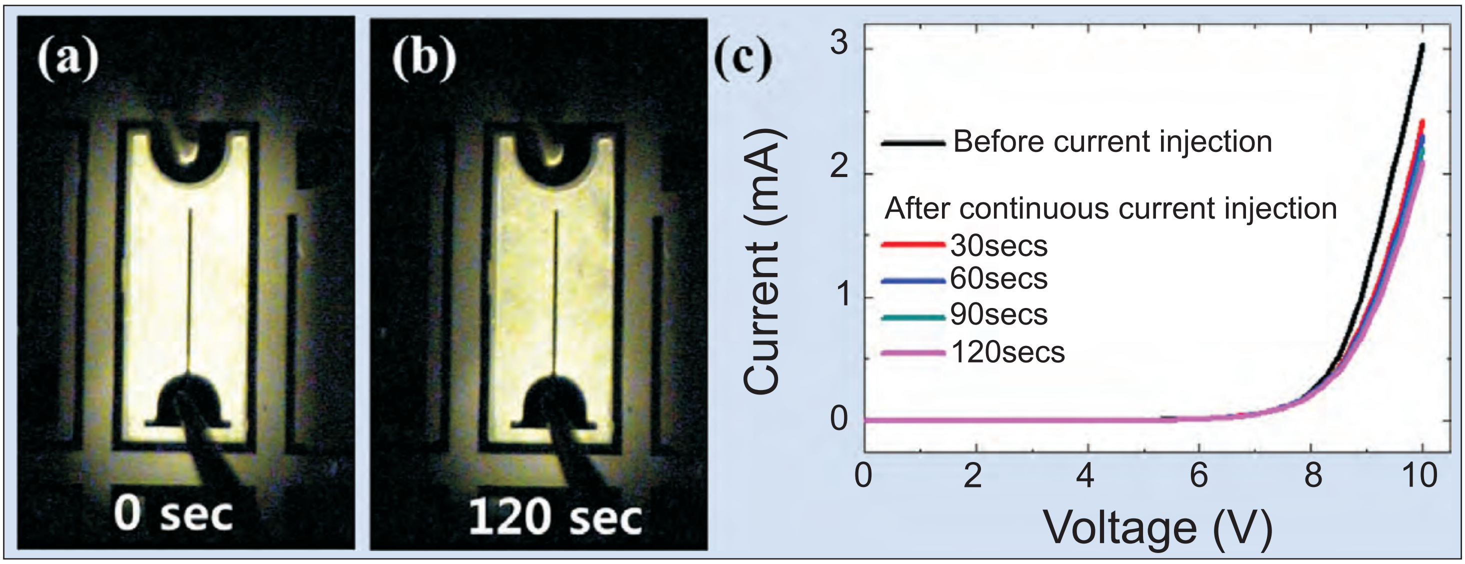

Figure 6. Microscopic electroluminescence images of UV-LED with SiN_x layer (a) before (b) after applying continuous current injection for 120s at forward bias of 10V. (c) I–V from UV-LED with SiN_x protective layer.

Institute of Semiconductors and Tsinghua University.

Although the use of graphene as TCL has begun to be explored recently, the application has generally been to more traditional lateral LEDs where the nitride epitaxial material remains attached to its sapphire growth substrate. In a lateral LED, the n- and p-type electrodes are on the same side of the device, away from the electrically insulating substrate. The current flow path is therefore partly lateral, as it flows through the LED to create light emission.

In the new research, the sapphire substrate was removed using a laser lift-off process to allow vertical current flow from n- and p-type electrodes on opposite sides of the LED chip. In theory, such an arrangement could allow much higher-performance devices, although there is some way to go to make such LEDs more competitive than their lateral counterparts.

One particular problem is the blocking of light output by the metal contacts used to deliver current to the devices. This could be improved by current-spreading layers to redistribute light output away from the contact region using TCLs.

In the new research, the epitaxial material was grown on sapphire using MOCVD (Figure 7). The u-GaN buffer was 2μm, the n-GaN contact was 5μm, and the p-GaN contact was 0.1μm. The multi-quantum-well active region consisted of 10 pairs of 3nm InGaN wells and 7nm GaN barriers.

After the epitaxial material was grown, a highly reflective metal was deposited on the p-GaN contact layer, followed by electro-deposited copper. The copper eventually became the substrate of the complete VLED. The original sapphire growth substrate was then removed using a laser lift-off process.

The graphene was grown on copper foil in a chemical vapor deposition process.

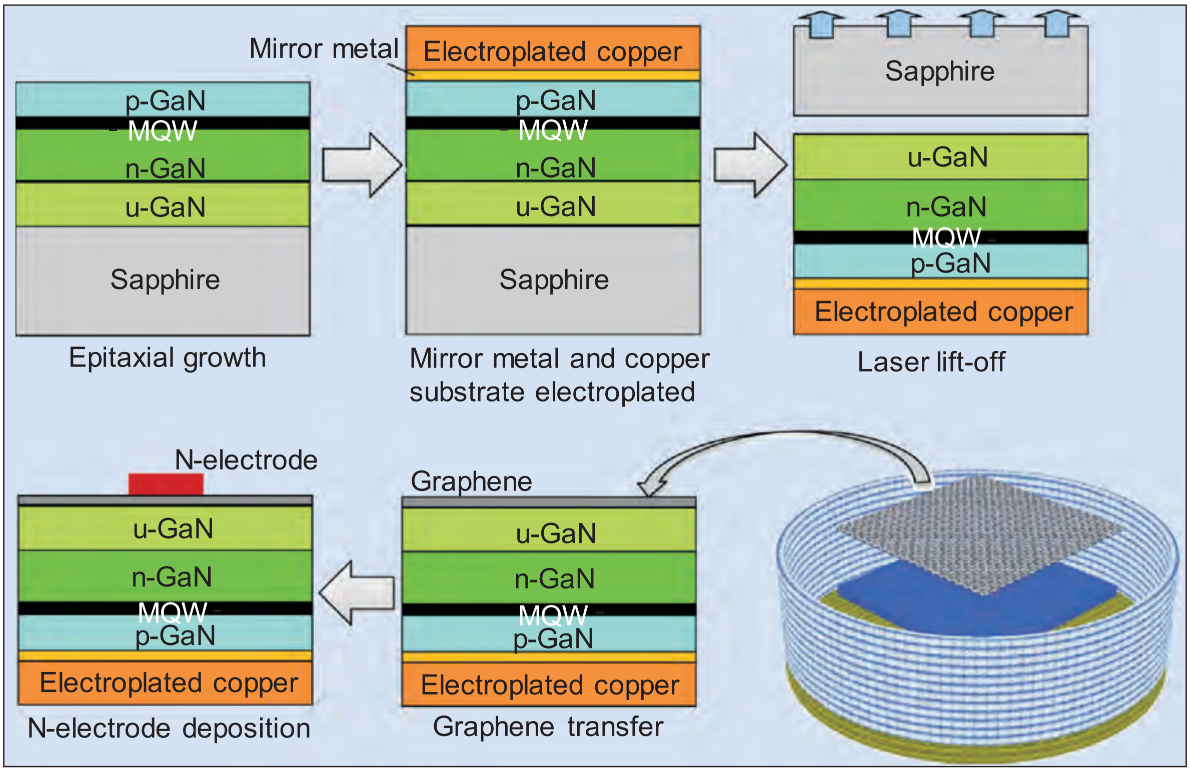

Figure 7. Schematic diagram of G-VLED fabrication process.

The foil was removed using iron chloride solution and the graphene was transferred to the flipped GaN layer of the VLED. After drying, the chromium/platinum/gold n-electrode was applied. The VLED chips were isolated and packaged before testing.

The researchers estimate that the resulting graphene consisted of 6 or 7 monolayers. The transmittance of the film was between 85% and 97% in the 400–800nm wavelength range. This compares with ITO with a transmittance in the same range of around 80%.

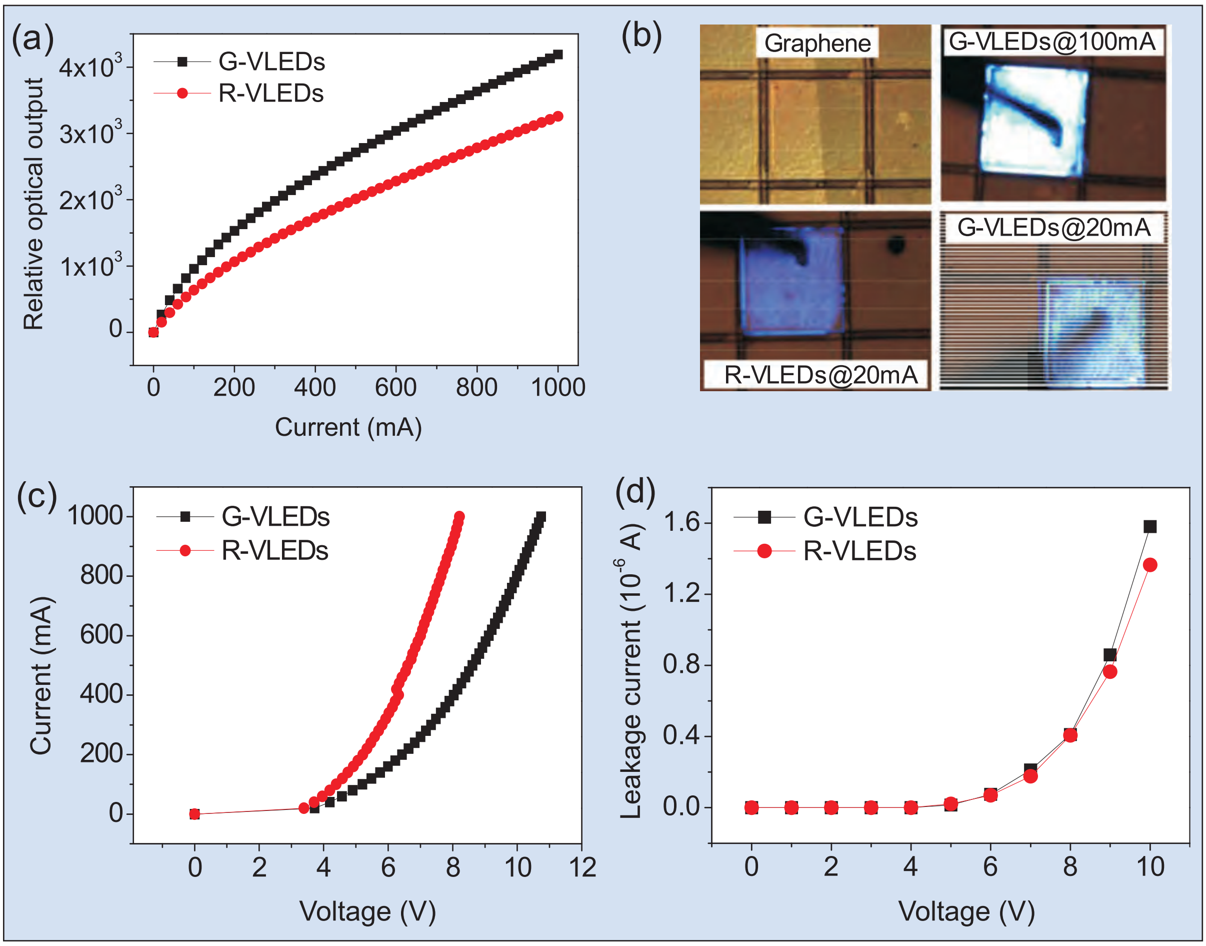

Figure 8. (a) Light output intensity vs current curve for G-VLEDs and R-VLEDs. (b) Emission graph of GVLEDs at different injection currents. (c) I–V characteristics of G- and R-VLEDs before annealing. (d) Reverse I–V curves of G- and R-VLEDs before annealing.

The result of using graphene (G-VLED) rather than ITO (R-VLED) is a 25% increase in light output (Figure 8). The researchers comment: "The light output improvement of G-VLEDs can be attributed to the higher conductivity of graphene than that of u-GaN. In addition, due to the injection current spreading characteristics of graphene, G-VLEDs have relatively uniform current distribution, preventing the current accumulating below the n-electrode."

At present, the drawback of graphene is a higher forward voltage than the ITO TCL devices (9.35V at 1000mA, compared with 8.21V). Higher forward voltage indicated higher series resistance and hence power efficiency losses. The source of the problem is that graphene has a higher contact resistance with u-GaN than ITO.

The forward voltage became higher with annealing. From their measurements, the researchers conclude: "Inter-diffusion of metal atoms and Ga atoms during annealing lead to the partially sandwiched graphene structure, which has been demonstrated to be helpful to improve the performance and reliability of G-VLEDs. It is suggested that more attention need to be paid to the inter-diffusion of metal atoms between metal pads and GaN, especially when graphene films are extensively used in LEDs as transparent electrodes."

Some improvement in light output was found with annealing due to higher resistance under the n-electrode spreading and increasing the current density away from the n-electrode that blocks light output.

A final interesting development is research from Taiwan suggesting a two-fold increase in internal quantum efficiency of nitride MQWs with a graphene surface layer [Huei-Min Huang, Appl. Phys. Lett., vol101, p061905, 2012]. The internal quantum efficiency was measured in a series of photoluminescence experiments at varying temperature.

The researchers from National Chiao Tung University and National Cheng Kung University suggest the effect may be due to a high density of free carriers between the MQW structure and the graphene layer providing a screening of the large polarization electric fields that occur in standard nitride semiconductor heterostructures. These polarization electric fields tend to hold the electrons and holes apart, reducing the amount of recombination into light/photons — often referred to as the quantum-confined Stark effect (QCSE). ■

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