Transparent conduction for nitride LEDs

Mike Cooke reports recent developments in transparent conducting materials.

Transparent materials that conduct electricity are clearly desirable for the many new applications that combine light emission/absorption with electronics such as flat-panel displays and touch screens. In the compound semiconductor world, solar cells and light-emitting diodes would also benefit from the use of such materials.

In nitride LEDs, efficiency droop effects at high current injection mean that there is an advantage to making the current as uniform as possible across devices [see March/April issue, page 100]. Bare p-type gallium nitride (GaN) semiconductor has a lower conductivity, tending to restrict the current path to regions near the metal electrodes/pads. This creates a non-uniform current density across the device.

One approach for transparent conduction is to use very thin layers of metal. However, as metal thins it also becomes less conductive. Heavily doped wide-bandgap oxides, such as alloys of indium oxide (In_2O_3) and tin oxide SnO_2, or zinc oxide (ZnO) are also transparent conductors. In fact, indium tin oxide (ITO) is widely used for flat-panel displays. Unfortunately, there are supply and consequent pricing concerns with the mass usage of indium. Instead, zinc oxide is being developed as a potential lower cost alternative across a number of applications.

In the past decade, graphene has emerged as another contender for such applications. In this article, we explore some recent developments in transparent conducting materials for LED applications.

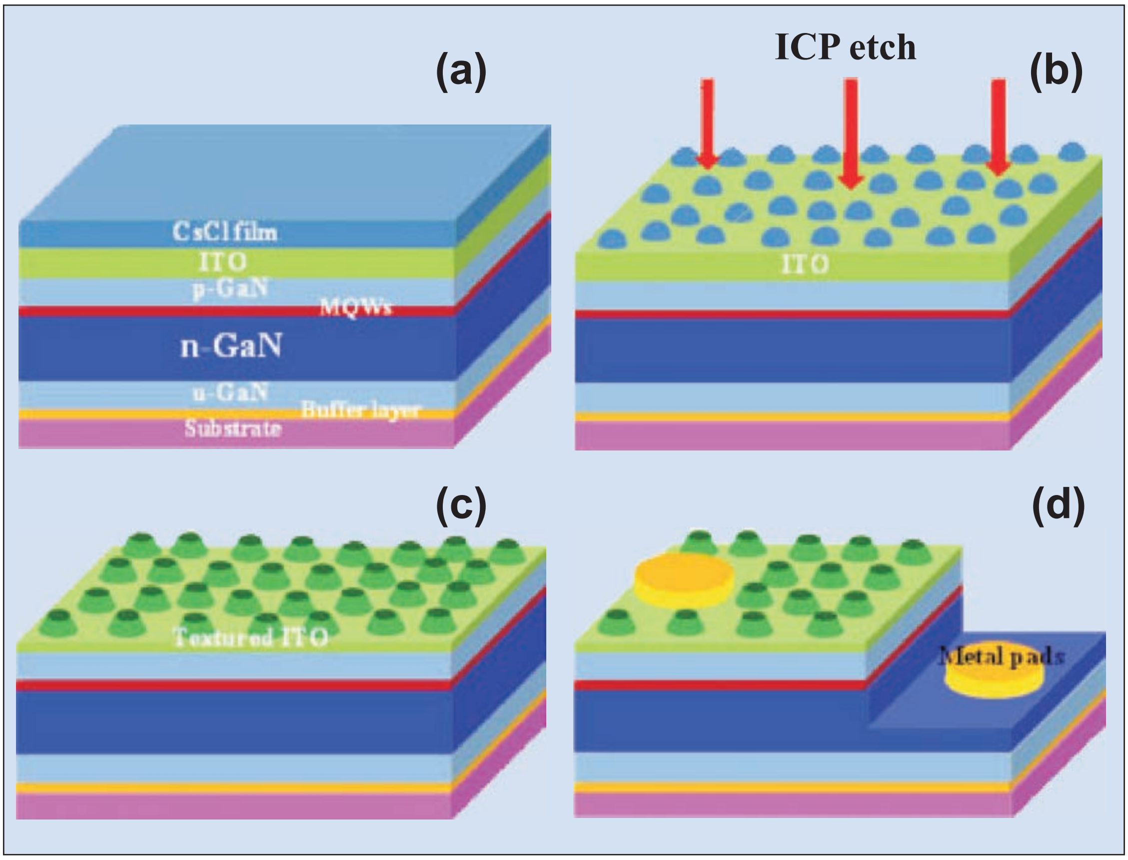

Figure 1. Schematics of Chinese Academy of Sciences fabrication process: (a) cesium chloride film deposition, (b) ICP etching, (c) nanoislands on the ITO layer, and (d) metal pad fabrication.

Nano-textured ITO

It is often helpful to light extraction to texture surfaces. This is because light is reflected back into the LED at interfaces between materials with different refractive indices, such as GaN/air or ITO/air. Researchers in China have used self-assembled cesium chloride (CsCl) nanospheres as a cost-effective mask for nano-texturing ITO layers on nitride semiconductor LEDs to improve light extraction by up to 23.4% [Yiyun Zhang et al, Jpn. J. Appl. Phys., vol51, p020204, 2012].

The researchers were based at Chinese Academy of Sciences' institutes of semiconductors (Semiconductor Lighting Technology Research and Development Center) and of high-energy physics in Beijing. Researchers from the same facilities had previously attempted to use CsCl nanospheres to nano-texture the p-type GaN layer of nitride LEDs directly, but found that the process often degraded the electrical performance of devices.

In the new work, conventional LED structures were grown on sapphire using metal-organic chemical vapor deposition (Figure 1). The active layer consisted of an 8-period multi-quantum well (MQW) with InGaN wells and GaN barriers.

A 300nm ITO transparent conducting layer was electron-beam deposited on the top p-GaN layer of the LED. This was followed by thermal evaporation of CsCl onto the ITO — various thicknesses of this layer were tested to optimize the process.

Exposure of the CsCl layer to water vapor caused the material to 'self-assemble' into 'nanospheres'. The spheres were randomly distributed on the wafer surface ($1.6–0.13x10^9/cm^2$). The average diameter of the spheres (450–900nm) is controlled by the CsCl film thickness (50–150nm), relative humidity, and development time. In fact, the 'spheres' were not spherical but rather approximately hemispherical — a 700nm-wide island had a height of around 300nm.

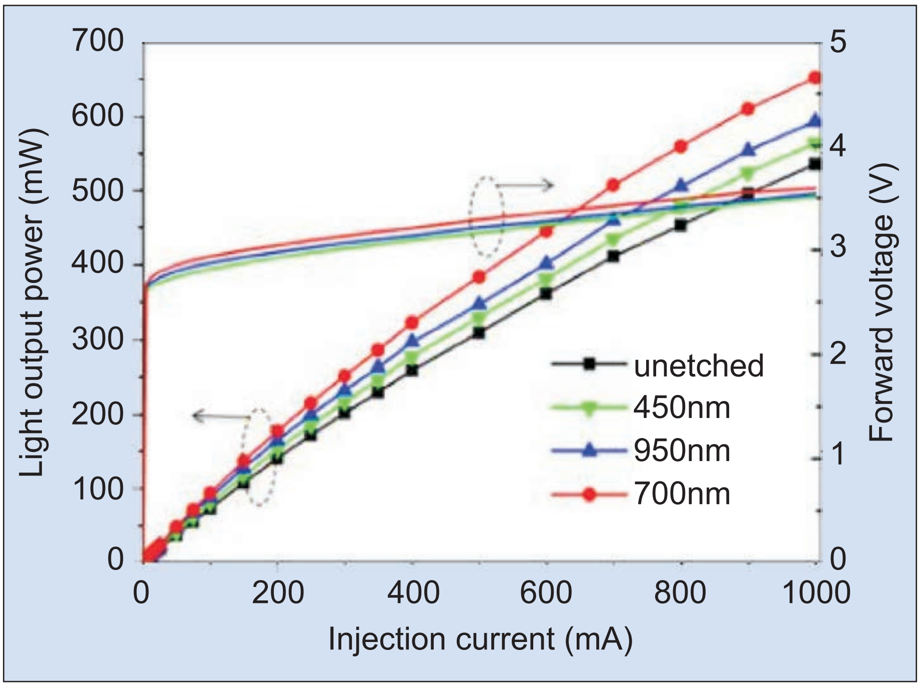

Figure 2. Light output power and forward voltage vs. current for LEDs produced by Chinese Academy of Sciences using different cesium chloride nanosphere sizes.

The wafer was then subjected to inductively coupled plasma etching to pattern the ITO surface. The CsCl residue was then removed by soaking in deionized water. This etch process textured the ITO surface into truncated-cone nanoislands.

LEDs were constructed from the resulting material by etching mesas and applying chromium/platinum/gold metal layers on the p- and n-type contact layers.

All the treated ITO surfaces showed improved light output power at 350mA over a planar device (Figure 2). The largest improvement of 23.4% came from the 700nm nanosphere etched surface. Improvements for 450 and 900nm nano-sphere treatments were 6.8% and 13.1%, respectively.

The researchers comment: "Obviously, there is an optimal size of the cesium chloride nanospheres. When the cesium chloride nanospheres are too large, the light scattering occurring at the interface between the ITO layer and the air will be reduced because of the fewer nanoislands fabricated on the ITO layer. On the other hand, too small cesium chloride nano-spheres cannot entirely cover the ITO layer, which strongly affects the surface morphology of the etched ITO layer."

An important further consideration is that the treatment has little impact on electrical performance, as seen in the very similar current–voltage curves (Figure 2). This allows the researchers to conclude that the electrical performance of the LEDs is not damaged by the etch process. However, there is a slight increase in forward voltage of 0.1V in the best light output power device from 700nm nanospheres. This could be due to the

Contact	Mg-doped p^+-GaN	10nm
Hole injection	Mg-doped p-GaN	50nm
Electron blocking (EBL)	Mg-doped p-GaN/p-AlGaN (15% Al)	16nm/16nm
Active	3x(GaN/InGaN) (15-20% In)	20nm/3nm
Electron injection	Si-doped n-GaN	1µm
Substrate	$(10\bar{1}\bar{1})$ bulk GaN	

Figure 3. Epitaxial structure used for UCSB/CNU LEDs.

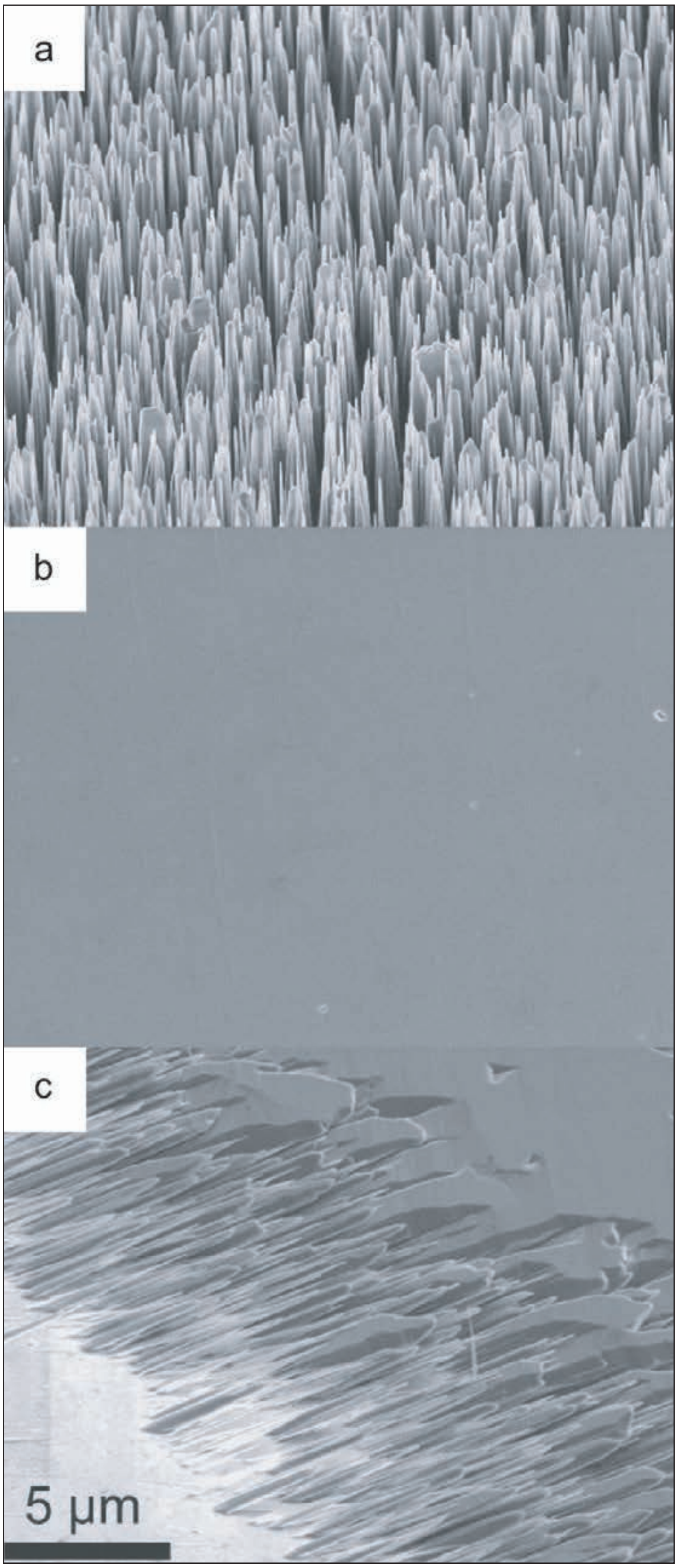

Figure 4. Representative SEM images showing the UCSB/CNU ZnO morphology resulting from identical growth conditions on (a) (0001) and (b) $(10\bar{1}\bar{1})$ GaN substrates. An uncoalesced region of the same $(10\bar{1}\bar{1})$ film from (b) is shown in (c).

surface being too rough to form good ohmic contacts on the ITO layer.

Zinc oxide

Researchers in the USA and Korea have been developing zinc oxide (ZnO) as a transparent conducting material for use with LEDs constructed from $(10\bar{1}\bar{1})$ semipolar nitride semiconductor material [Jacob J. Richardson et al, Appl. Phys. Express, vol4, p126502, 2011].

The use of semipolar or even nonpolar III-nitrides is designed to overcome polarization field effects that arise spontaneously and in strained piezoelectric conditions such as the quantum-confined Stark effect (QCSE). These fields are strongest along the standard c-direction of the nitride semiconductor lattice.

The University of California Santa Barbara (UCSB) has been researching semipolar and nonpolar devices for some time. The Korean researcher, Jun-Seok Ha, came from Chonnam National University (CNU), Republic of Korea.

The UCSB/Chonnam team grew their devices on $(10\bar{1}\bar{1})$ bulk GaN substrates supplied by Japan's Mitsubishi Chemical Corp. Atmospheric-pressure metal-organic chemical vapor deposition (MOCVD) was used to grow multiple films of various alloys involving indium, aluminum and gallium nitrides (InAlGaN — see Figure 3).

The ZnO transparent layer was grown using a low-temperature aqueous solution (pH 12 ammonia with dissolved ZnO). The substrates were suspended in the aqueous solution for 18 hours at 90ºC.

Unlike previous work with c-plane GaN, the researchers found that they did not need separate nucleation or 'seeding' steps or solution additives to modify the morphology. For the c-plane growth these extra steps/additives avoid the formation of needle structures, rather than the desired smooth coalesced film (Figure 4). Further study of the sample holder region (Figure 3c) suggested that the growth —even on the $(10\bar{1}\bar{1})$ — GaN starts as needles pointing in the c-direction, but that these needles then coalesced to form a smooth film.

Thicker layers of ZnO were applied in multiple steps. The first layer was annealed at 500ºC in oxygen–nitrogen (20% O_2) gas for 15 minutes to improve adhesion of subsequent layers. Without this annealing step, the entire film of thicker layer ZnO would occasionally delaminate.

LEDs were then created using standard processes such as chlorine plasma etch to the n-type layer, forming 2mm x 0.5mm mesas, and electron-beam deposition of the contact metals. The backside of the wafer was roughened to reduce light reflection at the sapphire–air interface. The singulated chips were packaged in a vertical stand transparent LED architecture.

Pulsed measurements (1% duty cycle, Figure 5) gave light output power of 27mW at a current density of $2A/cm^2$, and 276mW at $35A/cm^2$. The maximum external quantum efficiency (EQE) reached 48% at 1A/cm^2. At the highest current density of 35A/cm^2, this had fallen to 27.5%.

The researchers comment: "The light output and EQE of the device using the ZnO were lower than results previously published for a similarly packaged $(10\bar{1}\bar{1})$ device using an ITO current-spreading layer."

The team points out that, due to the smallness of the substrate available, they were unable to compare their ZnO-covered device with one using ITO. The difference in performance with the earlier experiment could be down to a difference in quality of the substrates or in run-to-run process variations in the MOCVD growth of the epitaxial material, they say.

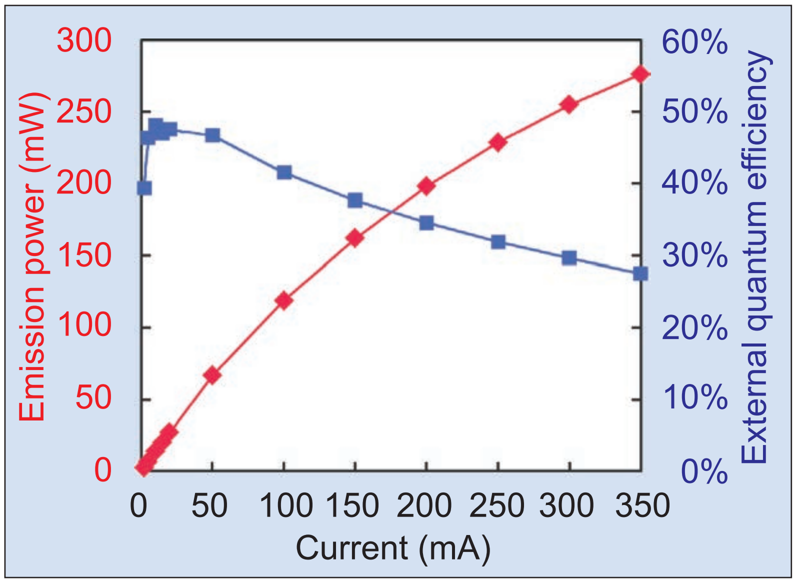

Figure 5. Light emission power and external quantum efficiency of UCSB/CNU semipolar $(10\bar{1}\bar{1})$ LED using an epitaxial ZnO current-spreading layer deposited from low-temperature aqueous solution. Measurements were performed under pulsed current conditions (1% duty cycle).

Monolayer graphene

Another group of Korean and US researchers has compared the performance of graphene with ITO as a transparent conducting electrode (TCE) on the p-contact of nitride semiconductor LEDs [Tae Hoon Seo et al, Jpn. J. Appl. Phys., vol50, p125103, 2011].

This research involved Chonbuk National University, University of Michigan (UM), and Sungkyungkyun University (SU), and used monolayer graphene grown on copper foil. Earlier last year, a different team of researchers from Korea University, Korea Electronics Technology Institute and US Naval Research Laboratory reported the use of few-layer graphene as TCE for UV applications (www.semiconductor-today.com/news_items/2011/NOV/KU_071111.html).

One particular attraction for graphene is that it transmits light of shorter wavelengths beyond the 300–400nm ultraviolet range where ITO cuts off. Comparisons between the light transmittance of graphene and 250nm ITO on aluminum oxide in the wavelength range 400–800nm gave values of more than 90% (up to nearly 97%) and ~80%, respectively. Below 400nm (the UV region), graphene continued to transmit about 90% of light, while ITO became opaque around 300nm.

One drawback of graphene is that due to its thinness it is more resistive than ITO. This means that the forward voltage at 20mA of the graphene contact LED was 5.87V, compared with 3.4V for the ITO-based device. Despite this, the light output power was 25% greater in the graphene LED at 20mA (Figure 6). The power loss of the graphene contact does begin to impact performance around 80mA, causing early saturation of device performance.

The researchers expect further efficiency enhancements in GaN-based LEDs that use graphene due to the intensive research in graphene material. This research is expected to allow enhanced electrical properties such as control of the graphene work function and reduction of sheet resistance.

The LED structures were grown on sapphire using MOCVD. The active layer was a five-period InGaN/GaN quantum well/barrier structure. The p-GaN layer was 200nm thick. The n-GaN layer was 2μm thick, grown on 2μm GaN buffer and 25nm GaN nucleation layers.

The high-quality monolayer graphene was produced using chemical vapor deposition on 70μm copper foil. After a preparatory flow of hydrogen to reduce oxide on the copper (2.5 hours), the carbon source of methane was introduced (30mins). To transfer the

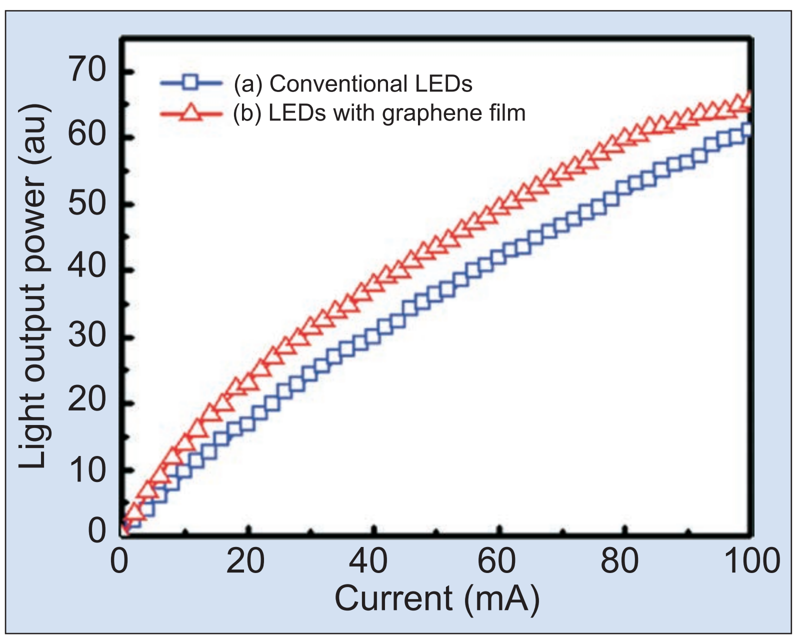

Figure 6. Light output of CNU/UM/SU LEDs versus current.

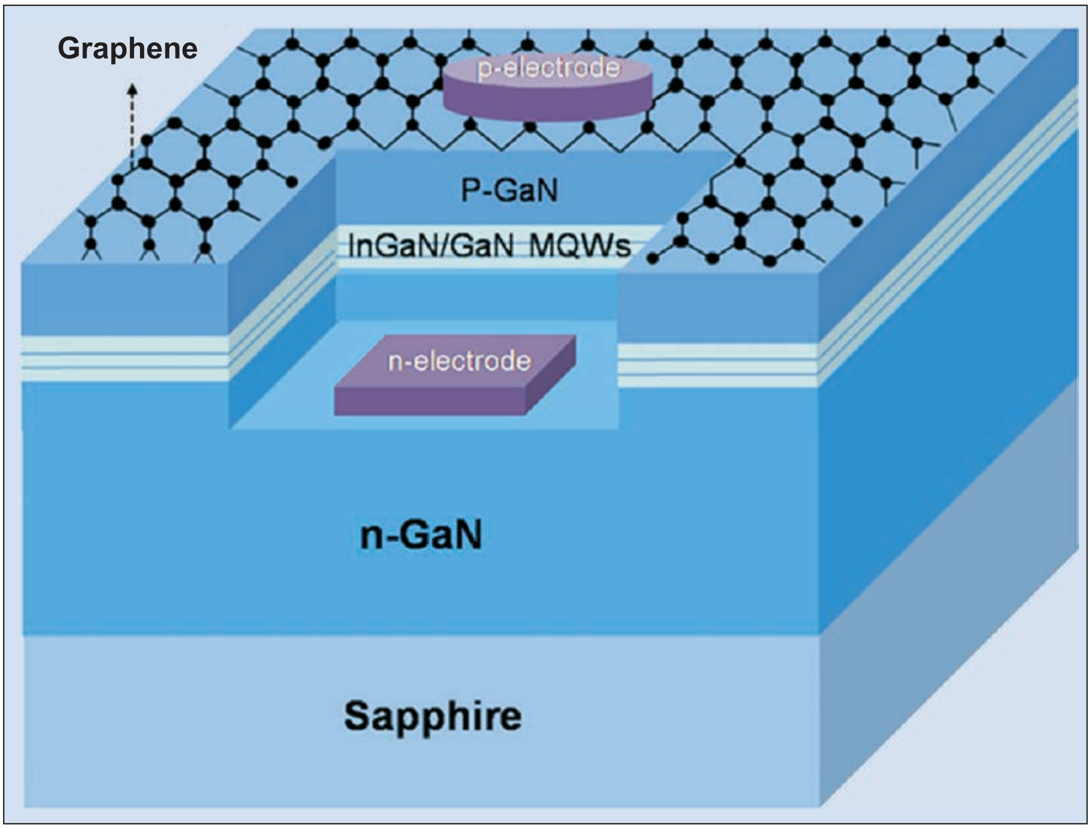

Figure 7. Schematic of CNU / UM / SU GaN-based LEDs with graphene film.

graphene, a poly(methyl methacrylate) (PMMA) film was spin-coated on the graphene. The copper was then (wet) etched away. The graphene was then applied to the GaN surface and the PMMA removed by annealing at 500ºC in a hydrogen/argon mix for 30mins.

The LEDs (Figure 7) were formed by creating a mesa, removing the graphene film in the n-electrode region using an asher and then plasma etching the nitride semiconductor material down to the n-type layer. The electrodes for the n- and p-layers were chromium/gold. Devices with 250nm ITO transparent conduction layers were also produced for comparison.

University of California Santa Barbara and University of Michigan have been researching the theoretical reasons for the UV cut-off in tin oxide [H. Peelaers et al, Appl. Phys. Lett., vol100, p011914, 2012]. The team sees free-carrier absorption (FCA) as being the fundamental source of optical loss giving a transparency limit.

Although FCA is usually considered an infrared phenomenon, the UCSB/UM research suggests that it can also be significant in the visible range. FCA is an indirect process involving additional processes such as coupling to lattice vibrations/phonons. The additional process is needed to conserve quasi-momentum in the conduction band (Figure 8). The work is based on first-principles density functional and perturbation theory.

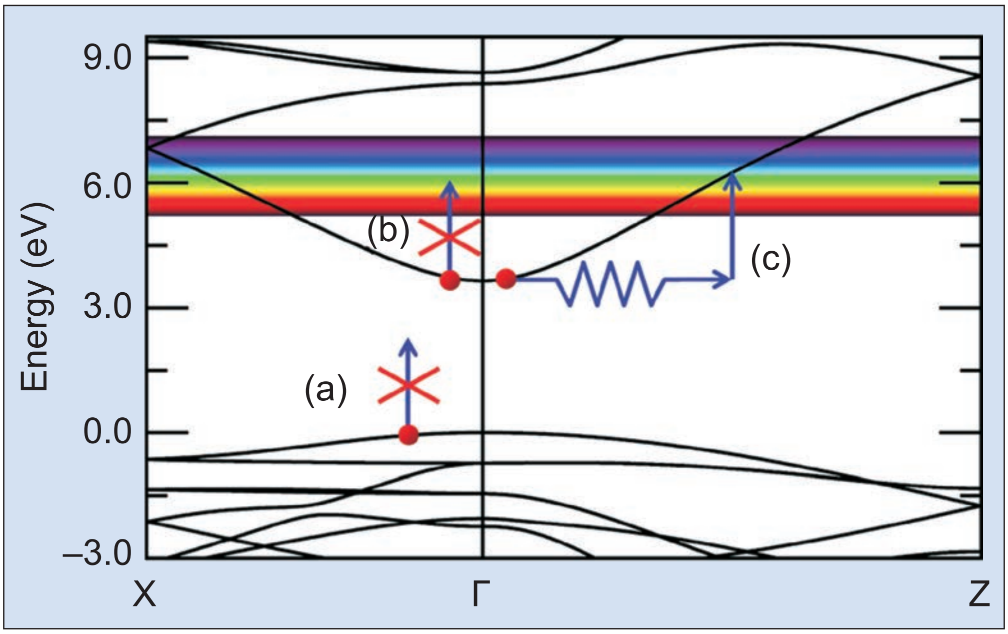

Figure 8. UCSB calculation of band structure of rutile SnO_2, illustrating free-carrier absorption. Visible light does not carry enough energy to excite carriers across the band gap (a) or to excite free carriers directly to the next conduction-band states (b). But extra momentum provided by a phonon enables indirect free-carrier absorption (c) for any visible or infrared wavelength. States in energy range of the visible spectrum are indicated.

In particular, the researchers see an absorption enhancement at short wavelengths (Figure 9), but before direct inter-band transitions are allowed. The tin oxide bandgap is about 3.6eV (344nm). Indium oxide has a similar value. However, these bandgap values are the least energy difference between the valence and conduction bands and do not represent dipole allowed transitions. The dipole allowed gap in tin oxide is 4.3eV (288nm). The researchers comment: "The absorption enhancement at shorter wavelengths cannot be described by simpler approaches such as the Drude model and is a clear prediction of our first-principles approach."

On the basis of their calculations, the researchers believe that electron–phonon scattering is the dominant mechanism in the 300–6000nm wavelength range, so long as the electron concentrations are under $10^{20}/cm^3$. At higher concentrations, scattering from ionized donors becomes significant in FCA. The absorption increases towards the UV and IR communication ends of the spectrum by up to 5x and 20x, respectively.

"Direct absorption of visible light cannot occur, because the next available electron level is too high in energy. But we found that more complex absorption mechanisms, which also involve lattice vibrations, can be remarkably strong," says Hartwin Peelaers, a postdoctoral researcher and the lead author of the paper.

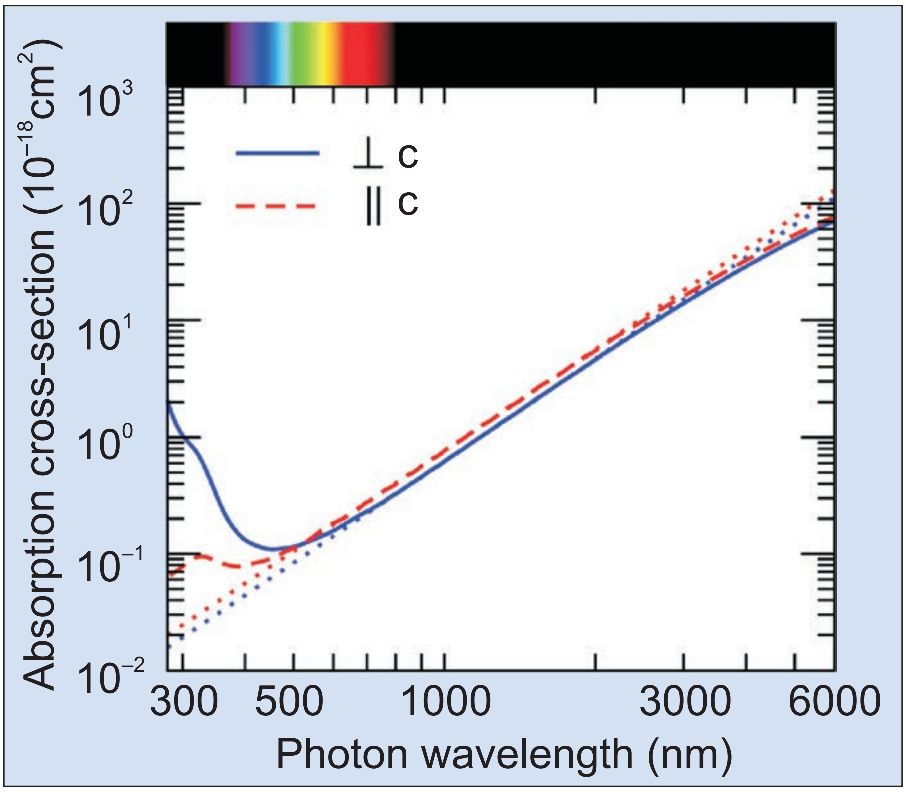

Figure 9. UCSB calculation of phonon-assisted free-carrier absorption in SnO_2 for light polarized perpendicular (solid line) or parallel (dashed line) to c-axis of the rutile structure. The dotted lines are fits to a simple model based on a Fröhlich electron coupling to longitudinal optical phonons. The visible spectrum is shown at the top of the graph as a reference.

Graphene-nanorod hybrid

Researchers in Korea have combined graphene (Gr) and zinc oxide nanorods (ZNRs) in a nitride LEDtransparent conducting layer (TCL) [Jung Min Lee et al, Appl. Phys. Lett., vol100, p061107, 2012]. The effect is to increase light emission, along with improving the electrical current injection performance of the device.

The research was an academic–industrial collaboration between Hanyang University (HU) and LG Display Co Ltd.

At 2.8V forward bias, an LED with Gr TCL demonstrated 4x the light intensity of a device without Gr, and 2x the injection current. Adding ZNRs gave a further 66% light output.

The researchers comment: "Our hybrid approach, which combines the key advantages of both 1D nanostructures and 2D Gr, could open up advanced and new design opportunities in high-performance optoelectronic devices resulting in optimal performance and functionality."

The base for the new device structure was a traditional InGaN LED with a trident-shaped p-electrode frame (Figure 10) to which a layer of graphene was applied. The graphene was produced by methane-based chemical vapor deposition on copper and

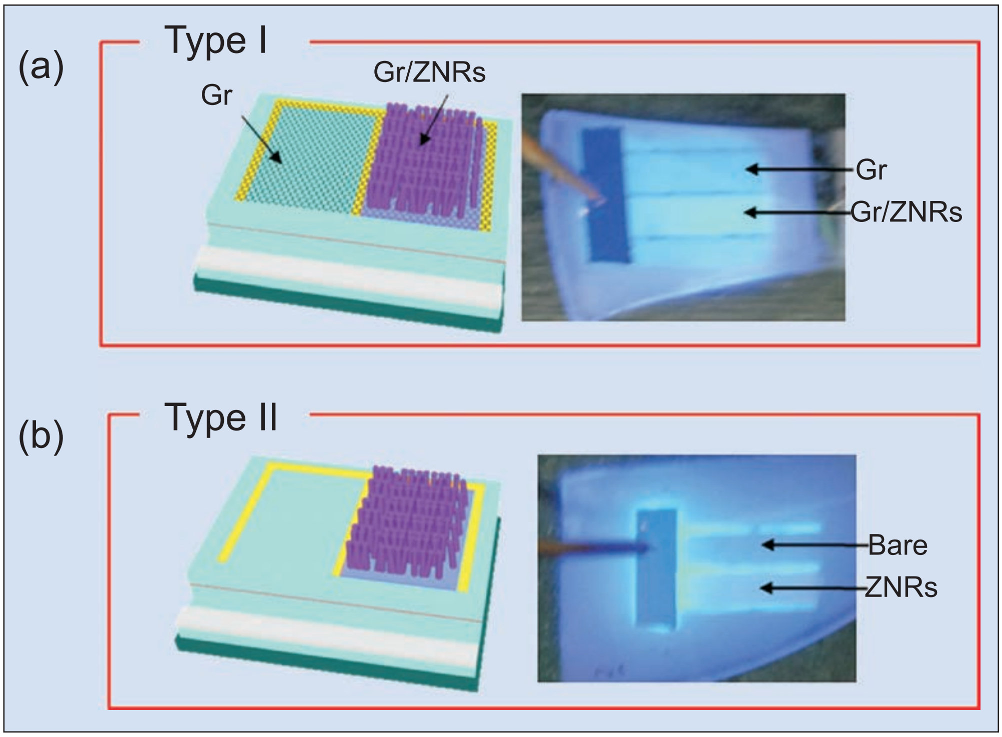

Figure 10. Schematic diagrams and photographs of HU/LG type I and II LEDs. (a) The schematic of type I LED with Gr and Gr/ZNR window electrodes along with a photograph of the resulting device. (b) The schematic of the type II LED with bare and ZNR window electrodes along with photograph of resulting device.

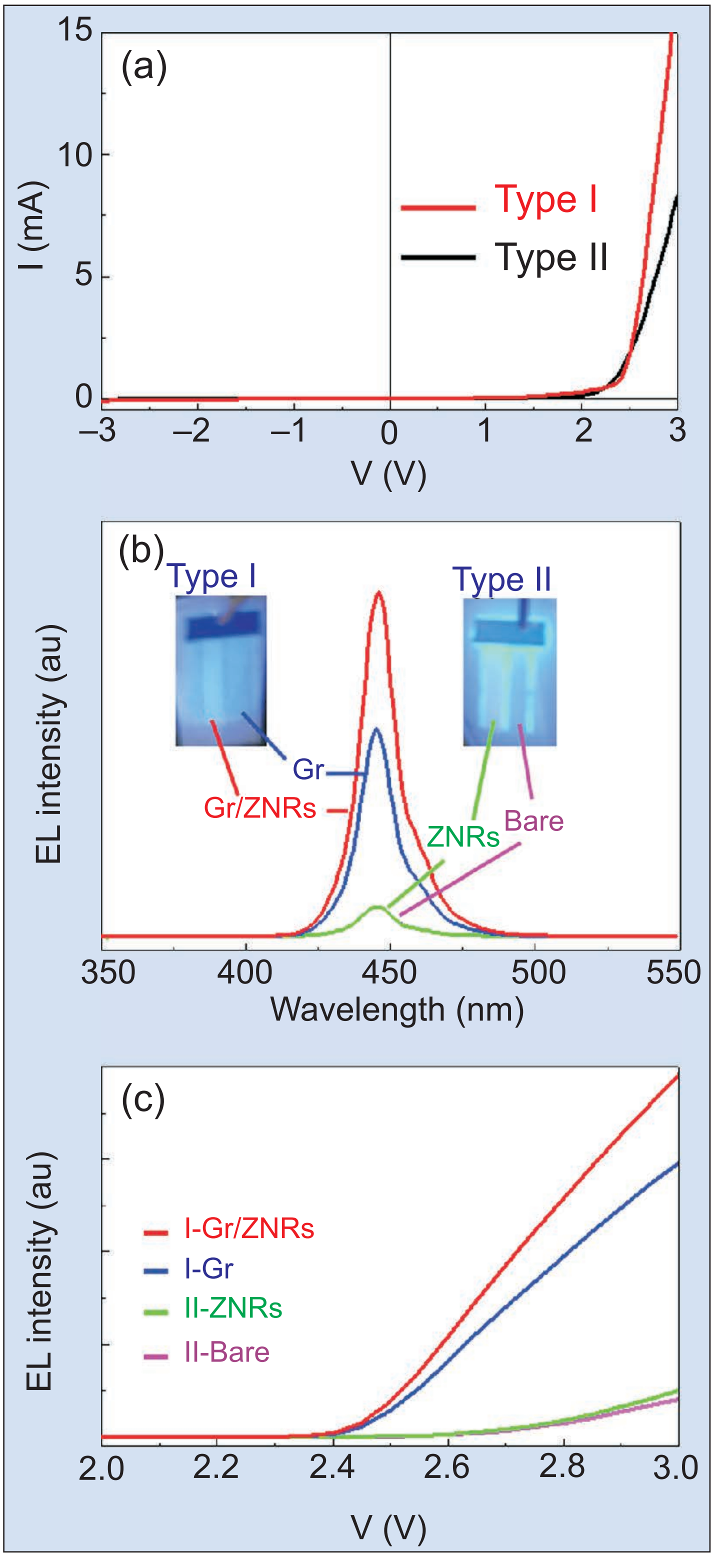

Figure 11. (a) Current–voltage (I–V) curves of HU/LG type I and II LEDs. (b) EL spectra of the type I and II GaN LEDs with four different top window electrodes (I-Gr, I-Gr/ZNRs, II-bare, and II-ZNRs) recorded at an applied voltage of 2.8 V. (c) EL intensity vs. voltage curves of GaN LEDs with different window electrodes.

transferred to the LED surface. ZnO nanorods were then grown selectively on the graphene using a low-temperature hydrothermal process in aqueous solution.

Optical experiments on the graphene and ZNR–graphene hybrid films suggested transmittances of 97% and 90% in the visible spectral range, respectively. The contact resistance was improved by including a very thin annealed layer of 1nm/1nm nickel/gold (Ni/Au) film before the ZNR–graphene hybrid film. The specific contact resistivity was reduced from 5Ω-cm^2 to 0.5Ω-cm^2 by the Ni/Au inclusion.

In all, four types of TCLs on the p-electrode were produced: a bare control, a ZNR-only film, a graphene film, and the ZNR-graphene hybrid. These were doubled up on two devices: 'type I' containing Gr-only and Gr–ZNR hybrid layers, and 'type-II' with bare and ZNR layers.

Scanning electron micrograph (SEM) inspection of the ZNR–graphene hybrid gave an average diameter for the near-vertical ZNRs of 50nm and an average height of 3μm. The hexagonal cross-section of the rods was taken as indicating high crystal quality. There was also observed a thin 50nm ZnO film immediately above the graphene and below the NRs. This thin layer is believed to act as a seed layer for the rods.

The turn-on voltages of the devices are around 2.5V (Figure 11a). At –3V reverse bias, the leakage current is 7x10^{-5}A. Under higher forward bias, the graphene-containing devices ('type-I') carry more current due, it is thought, to more efficient current spreading by the graphene and thin metal layers.

Electroluminescence occurred around the blue-violet wavelength of 446nm (Figure 11b). When driven at 2.8V, the current of the graphene-containing devices was double that of the non-graphene devices ('type-II').

In terms of light emission, the devices with graphene transparent contact exhibit up to 4x the amount of light intensity. Part of the improvement is attributed to reduced current crowding, giving more uniform illumination across the device. The improvement comes despite the estimated optical transmittance reduction of 20% due to the presence of the metal layers between the nitride contact and the graphene layers.

Adding the ZNRs, increases the light intensity a further 66% over the graphene-only device. This improvement is attributed to multiple photon scattering and the more gradual change in refractive index between the GaN layer and air. ZNRs have also been used to improve light extraction with ITO TCLs, giving a 57% boost with well-aligned rods and 34% for poorly aligned structures.

The better performance of ZNRs on graphene is attributed to the chemical stability of graphene. With ITO layers, the ZNR hydrothermal process attacks the TCL, slightly degrading its electrical properties.

The researchers also point to the better thermal properties of graphene for conducting heat away from the LED, improving performance. ■

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