Silver nanowires and compound semiconductor optoelectronics

Mike Cooke **reports on recent research into transparent conducting layers that incorporate silver nanowires as a possible replacement for indium tin oxide.**

A large range of electronics chemical suppliers offer silver nanowires in various solvents — water, ethanol, isopropyl alcohol, etc. These companies market AgNWs mainly for touchscreen and other transparent conductive electrode (TCE) applications offering flexible electronics. Recent research has focused more generally on the possibility of using AgNWs to replace expensive indium tin oxide (ITO) TCEs.

The AgNW solutions are generally spin-coated onto target device structures. Spin-coating could be a low-cost alternative to TCE processes using ITO or more complex techniques such as graphene deposition on metal foil and transfer. Although AgNWs potentially suffer from long-term stability/degradation problems, these could be overcome with suitable encapsulation and packaging.

Here we look at attempts to combine AgNWs into TCE structures for compound semiconductor optoelectronics.

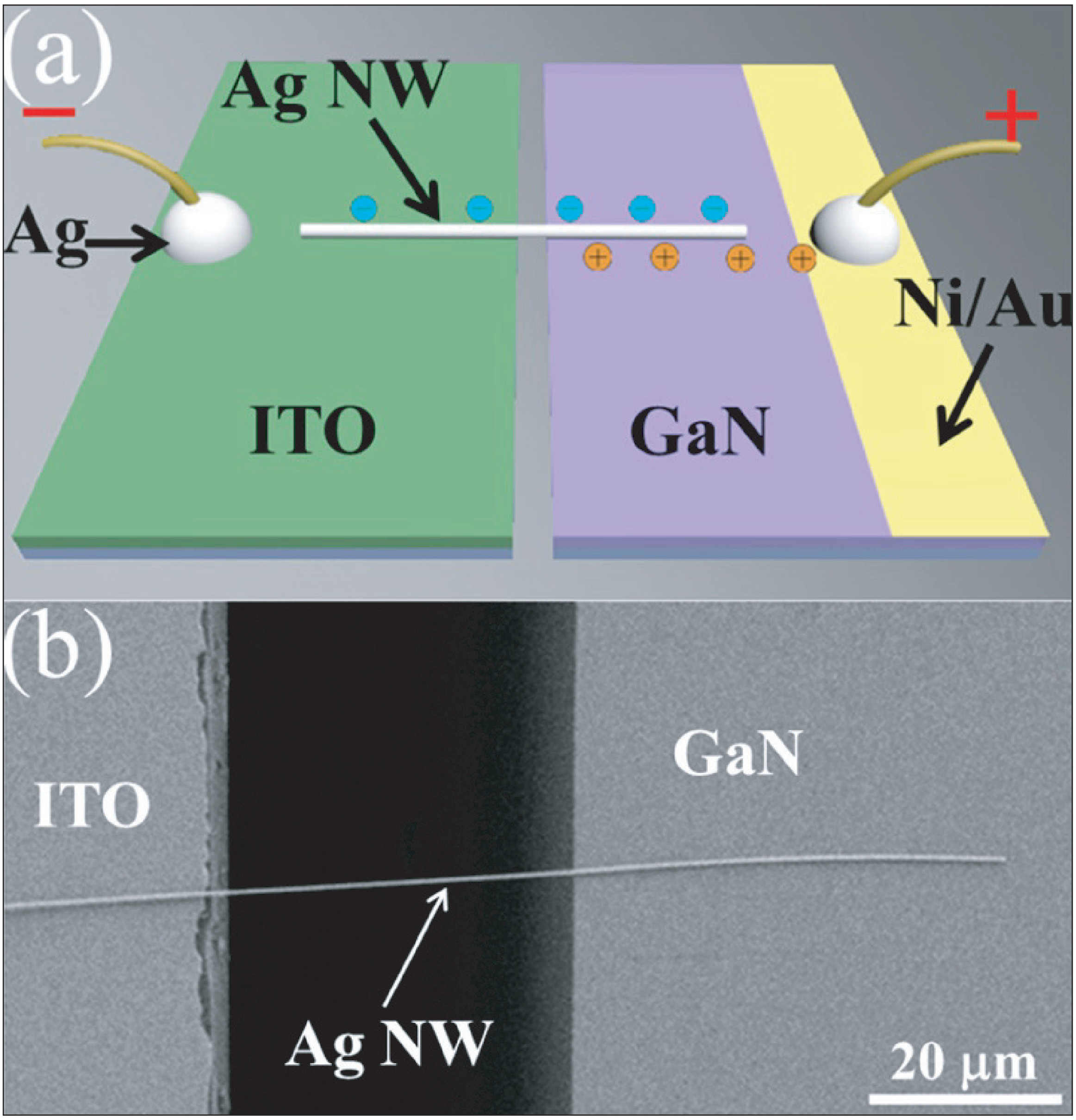

Figure 1. (a) Single AgNW/p-GaN ST-LED. (b) SEM image of as-fabricated device.

Schottky UV-LEDs

China's Zhejiang University and the UK's University of Cambridge have jointly developed ultraviolet light-emitting diodes (UV-LEDs) based on metal-semiconductor

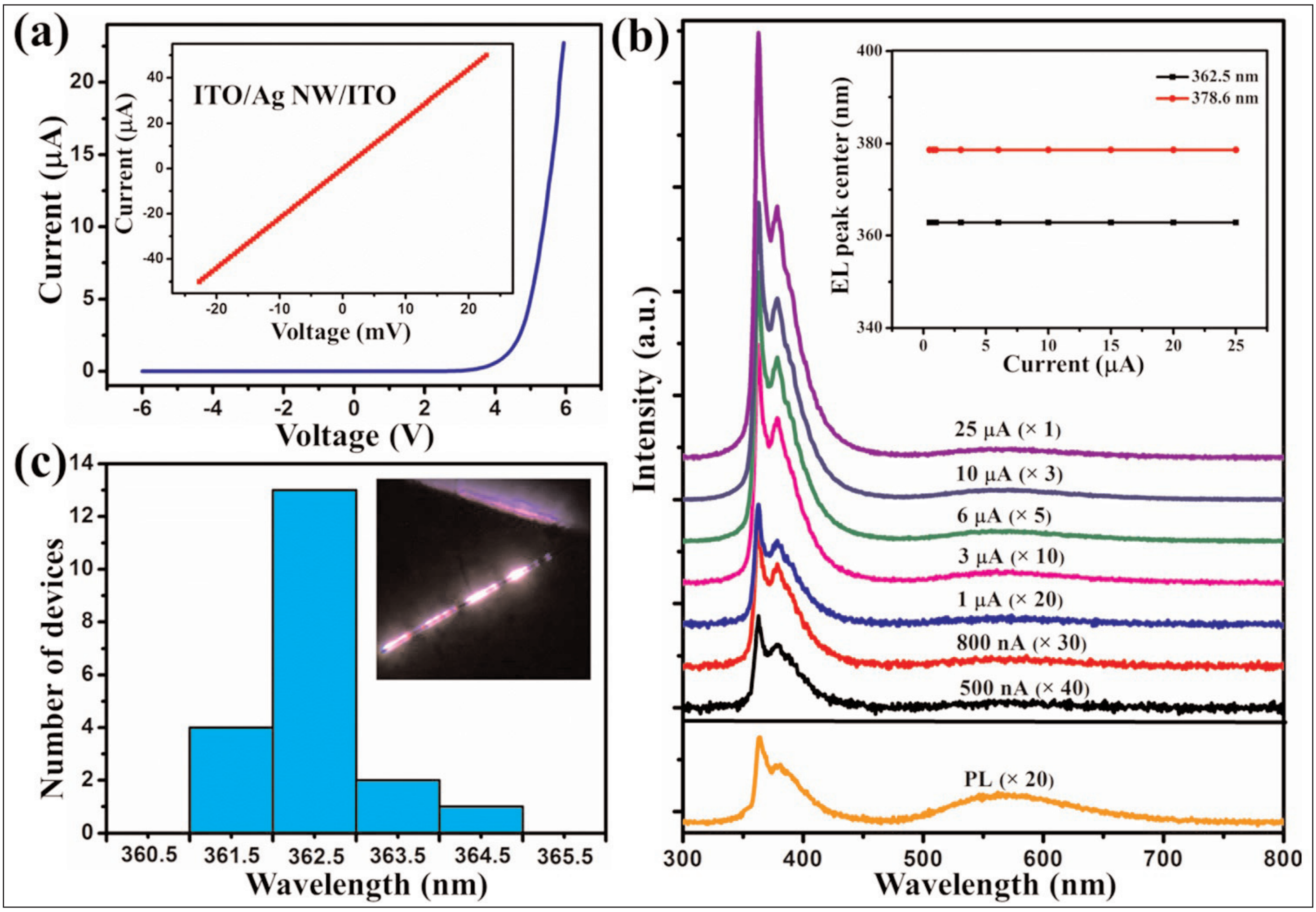

Figure 2. (a) Current versus voltage (I–V) characteristics of an as-fabricated device. Inset: ohmic contact behavior of ITO/AgNW/ITO structure. (b) EL spectra of device under various injection currents and the photoluminescence (PL) spectrum of p-GaN under 355nm pulsed laser excitation. Inset: EL peak position (362.5nm and 378.6nm) versus different forward currents of same device. (c) Dominant emission peak distribution of 20 devices. Inset: typical optical microscope image of emission.

Schottky junctions between silver nanowires (AgNWs) and gallium nitride (GaN) [Y. Wu et al, Appl. Phys. Lett., vol106, p051108, 2015].

The external quantum efficiency (EQE) for radiation around 362.5nm wavelength was as high as 0.9%. The researchers comment: "The EQE of our device is the highest reported to date for UV LEDs based on a Schottky junction."

UV-LEDs are being developed for a wide range of applications such as high-density information storage, water purification, the disinfection of medical tools, UV curing, phototherapy, and medical diagnostics.

The researchers see three advantages of Schottky-type LEDs (ST-LEDs) over conventional multiple quantum well (MQW) devices: "First, ST-LEDs do not require complex processing such as those required for MQWs. Second, the device operation does not rely on a p–n junction, reducing the difficulties associated with doping of semiconductors. Finally, it does not require the deliberate introduction of an intrinsic layer to reduce leakage current and to accumulate carriers near the interface, which is a key process in [metal-insulator-semiconductor] MIS LEDs."

Conventional ST-LEDs suffer a tradeoff from the metal layer absorbing a significant percentage of the LED output, reducing overall efficiency. The use of nanowires reduces this blocking of radiation.

The Zhejiang/Cambridge devices have a simple structure (Figure 1) that the researchers believe has "the potential to be a cost effective alternative to traditional UV-LEDs and can also be integrated into nano-optoelectronic systems".

The semiconductor material for the device was p-GaN grown on sapphire by metal-organic chemical vapor deposition (MOCVD). The diode fabrication began with cleaning and etching to remove native oxide from the GaN surface. After rinsing and drying, the nickel/gold p-electrode (anode/p-contact) was deposited by thermal evaporation. The cathode (n-contact) was an indium tin oxide (ITO) covered sapphire substrate micro-manipulated to give a gap of less than 0.35μm from the GaN substrate.

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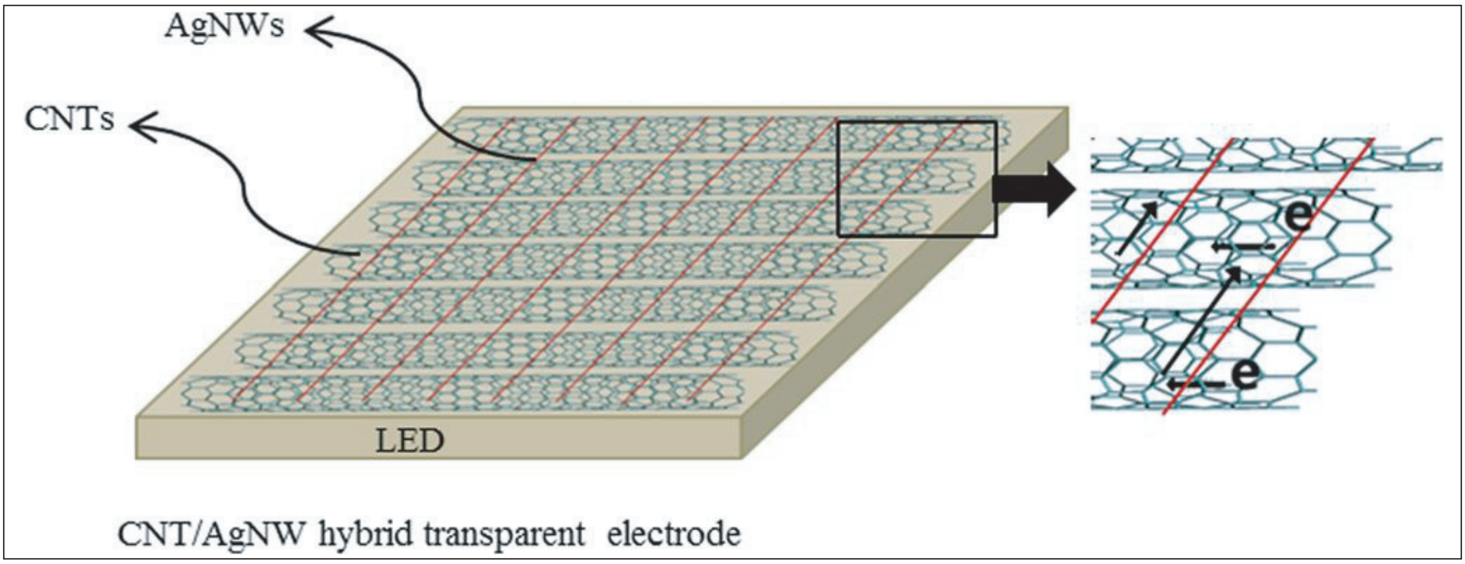

Figure 3. Schematic of LED with CNT/AgNW hybrid film as transparent conducting layer.

The gap between the p-GaN and ITO was bridged by silver nanowires produced by 'soft self-seeding'. The nanowires were generated from silver nitrate reduced with ethylene glycol (EG) in the presence of polyvinyl pyrrolidone (PVP). The resulting wires had a diameter of 120–500nm and a length of more than 50μm. The nanowires were purified in several cycles by immersing in ethanol, centrifuging and then rinsing in deionized water.

The nanowire suspension was deposited on clean glass. Single nanowires were then transferred to bridge the gap between the ITO and GaN substrates. The AgNWs were held in place by van der Waals forces.

The current–voltage curve of the device was rectifying with a forward bias onset at 4.8V (Figure 2). The silver-ITO and GaN-nickel/gold contacts were found to be ohmic in separate tests. The diode behavior was therefore a result of the Ag/p-GaN contact.

Electroluminescence (EL) was observed for forward currents as low as 500nA. The UV emission included two contributions: a main peak at 362.5nm with 7nm full-width at half maximum (FWHM) and a second peak at 378.6nm with 30nm FWHM.

The researchers attribute the main peak to recombination through an exciton state (electron–hole bound state). The second peak was assigned to isolated magnesium atoms from the p-GaN doping. There was also weaker defect-related emission from the visible range 480–710nm.

Much of the emission was trapped in the GaN because of total internal reflection from the GaN/air interface refractive index contrast. Trapped light was emitted from the edge of the device. The light output intensity increased as a 1.24 power of the current injection. The 'superlinear' behavior of the intensity is attributed to the changing balance of radiative and non-radiative recombination mechanisms. At 25μA injection the EQE was estimated to be 0.9%.

The team attributes the relatively high efficiency to the reduced blocking of the light by the nanowires compared with the usual metal electrodes. "The performance is also comparable to those of UV-LEDs based on NW/thin film p-n hetero-/homo-junctions and MIS junctions, with a simpler device architecture and potentially lower fabrication cost," the researchers add.

The highest efficiency was obtained for nanowires of 250nm diameter. Beyond that self-heating effects reduced the performance to 70% of the maximum EQE with 170nm diameter. (The current injection was not pulsed to avoid self-heating effects.) Narrower wires are less able to transmit heat away from the AgNW/GaN junction.

Enhancing carbon nanotube layers

Researchers in China have developed a hybrid AgNW/carbon nanotube (CNT) current spreading layer for aluminium gallium indium phosphide (AlGaInP) LEDs [Bai Liu et al, Appl. Phys. Lett., vol106, p033101, 2015].

The team based at Beijing University of Technology, Beijing University of Chemical Technology and Tsinghua University used the AgNWs to redistribute carriers between the CNTs (Figure 3). Without the NWs, the rate of carrier transfer between CNTs is low due to a high inter-tube contact resistance.

The researchers comment: "The hybrid film takes advantage of the extremely high mobility and conductivity of individual CNTs and avoids the high inter-tube contact resistance of CNT networks by including AgNWs. The carriers are not only transported along the CNTs but also between CNTs through the AgNW bridges in a vertical direction, providing a symmetric carrier distribution."

The AlGaInP LEDs consisted of an 800nm active region with 60-period $(Al_{0.5}Ga_{0.5})_{0.5}In_{0.5}P/(Al_{0.1}Ga_{0.9})_{0.5}In_{0.5}P$ multi-quantum well. The active region was sandwiched

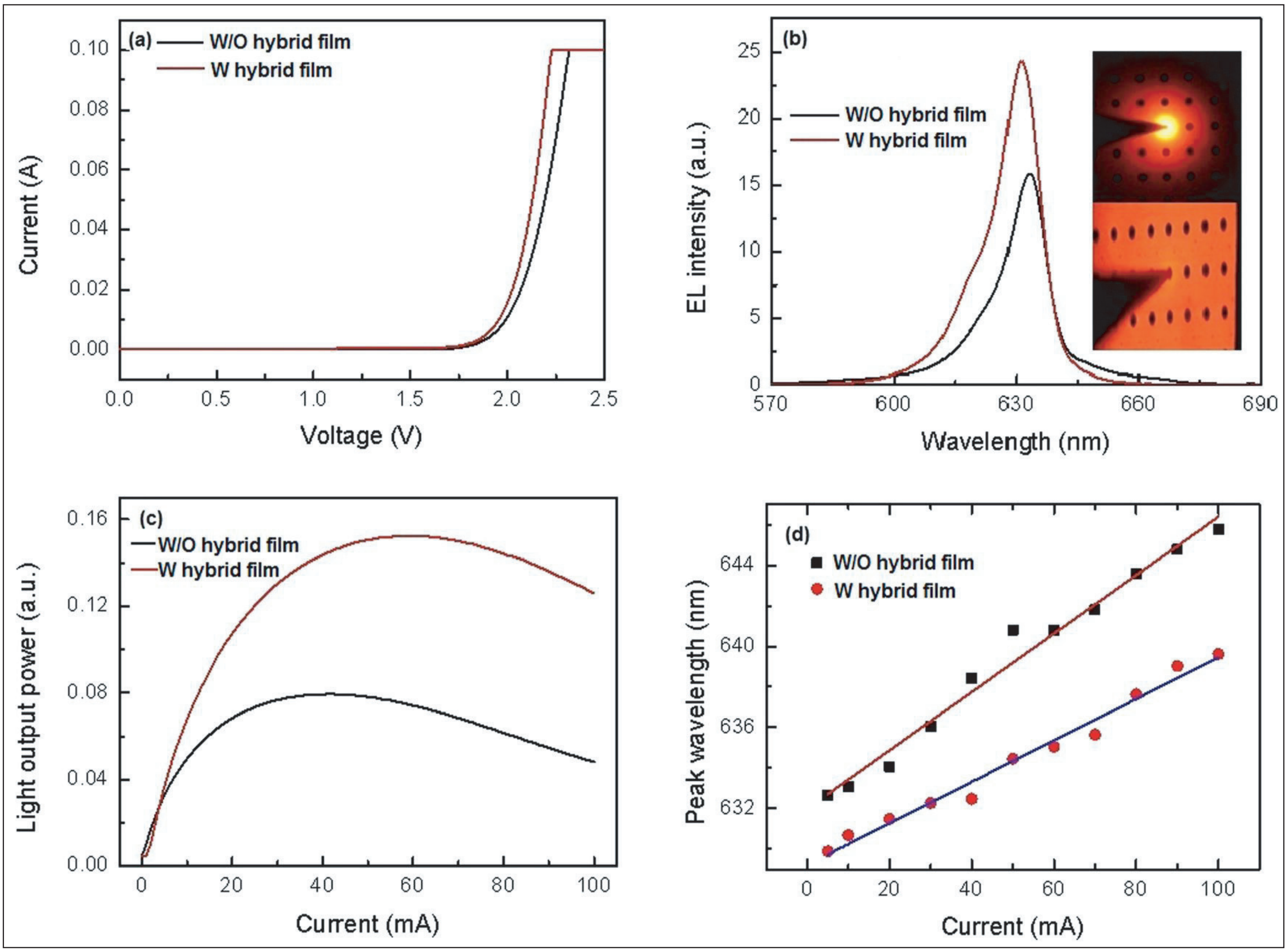

Figure 4. (a) Current versus voltage, and (b) EL spectra at 20 mA (inset: EL images at 2.5mA of 2.5µmx2.5µm area around electrodes of control and hybrid-film LED wafers), and dependence of (c) light output, and (d) peak wavelength on injection current of AlGaInP LEDs with and without AgNW/CNT hybrid film.

between n- and p-type cladding layers of $(Al_{0.7}Ga_{0.3})_{0.5}In_{0.5}P$. The LED heterostructure was grown on a distributed Bragg reflector consisting of 15 layer pairs of $Al_{0.6}Ga_{0.4}As/AlAs$ on a 100nm gallium arsenide (GaAs) buffer. The growth substrate was n-GaAs. The structures also included a final 500nm p-GaP window layer.

The p-electrode consisted of a 100µm-diameter region of gold/beryllium-gold/gold. The n-electrode was gold-germanium-nickel/gold sputtered onto the backside of the growth substrate. The CNTs were drawn continuously from multi-walled CNT arrays, adhering through Van der Waals forces. The process resulted in ‘a super-aligned CNT (SACNT) film’, according to the researchers. Titanium/gold was deposited and patterned on the p-electrode to make sure the SACNT film remained in place. The resulting LED chips were 300µmx300µm.

Optical transmission of 550nm wavelength through the SACNT was about 85%. To increase the light transmission the researchers used a 30-second oxygen plasma etch to decrease the density of tubes, increasing transmission to 96%. After the etch, the AgNWs were spin-coated onto the CNTs. The structure was then annealed at 200ºC for 10 minutes to improve the electrical contact between the AgNWs and CNTs.

By varying the AgNW concentration in the spin-coating process, the light transmission (T_{550nm}) could be traded off against sheet resistance (R_s). “For AgNW concentrations of 0.25mg/ml and 0.5mg/ml, T_{550nm} (R_s) of the hybrid films was 93% (88Ω/square) and 90% (23Ω/square), respectively,” the researchers report. The sharp drop in resistance is attributed to a typical percolation threshold effect, where a small increase in connectivity of a random network creates conduction paths across a space.

One effect of the AgNW/CNT hybrid film was to slightly reduce the LED forward voltage at 20mA from 2.1V to 2.0V (Figure 4). This indicates a reduced series resistance loss.

The electroluminescence was ‘greatly enhanced’ at 20mA by the presence of the hybrid AgNW/CNT current-spreading layer, despite an estimated 10%

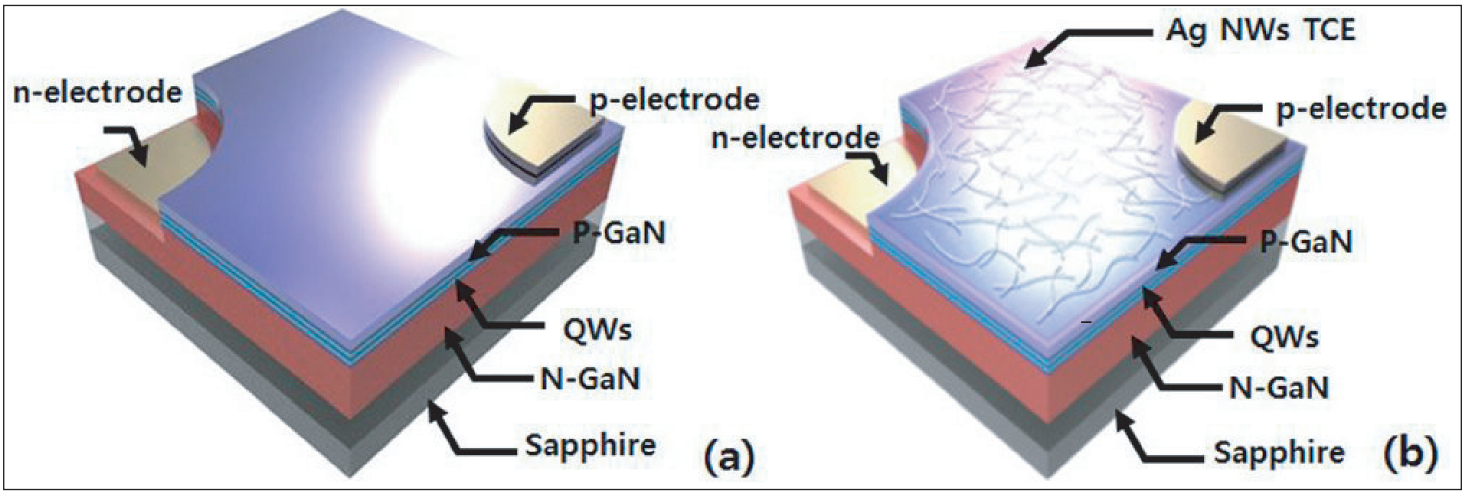

Figure 5. Schematics of conventional InGaN LED (a) and LED with AgNWs as transparent conductive electrode (b).

optical loss. The researchers add, "The high surface roughness of the hybrid film further increased the light output of the LED." This was presumably due to better transmission of light — rather than reflection — from the device-air interface.

The emission pattern of the LED chip without hybrid film showed current crowding around the p-electrode. By contrast, the emission from the LED with hybrid film was bright and uniform across the chip. The integrated intensity of the hybrid-film LED was 1.6x that of the control device at 20mA. The 1.6 enhancement factor continued up to 60mA injection. Beyond that the enhancement was limited by self-heating effects. The researchers say the current spreading effect was reduced by the higher temperature in the film.

With increased current injection, the emission peaks of both devices red-shifted — at the rates 0.1nm/mA and 0.15nm/mA for the hybrid-film and control devices, respectively. At 100mA, the corresponding total redshifts were 9.7nm and 13.11nm.

InGaN LEDs

Researchers have also investigated the use of just AgNWs as TCE. In Korea, a team based at Korea Polytechnic University and Chonbuk National University has used spin-coated AgNWs to improve the performance of InGaN LEDs [Gyu-Jae Jeong et al, Appl. Phys. Lett., vol106, p031118, 2015].

The researchers say that before their work "there have been no reports detailing the use of only AgNWs in GaN-based LEDs as TCEs, with the exception of graphene/AgNW hybrid films." The team believes improved LED performance was due to better current spreading and thermal dissipation via the AgNWs.

The InGaN heterostructures were grown on sapphire by metal-organic chemical vapor deposition. The LED material consisted of a GaN buffer (2μm) and n-contact (3μm), 5-period $In_{0.15}Ga_{0.85}N$ wells in GaN barriers, and GaN p-contact (0.1μm).

The epitaxial material was fabricated into 'ultra-large-size' 5mmx5mm mesa-structure LEDs (Figure 5). Conventional mesa-LEDs typically measure on the order of 1mmx1mm. The electrodes consisted of indium/tin.

The AgNWs were spin-coated for 40 seconds at 800 rotations per minute from a suspension supplied by Korean company Nanopyxis Inc [http://nanopyxis.com]. The nanowire source solution was sonicated for 6 minutes and shaken well before application. The deposited film was annealed for one minute at 100ºC, giving a sheet resistance of 15Ω/square.

The researchers report that the coating process resulted in networks of randomly oriented AgNWs with less than 50nm height variation — "sufficiently planar to form a p-type electrode in LEDs". The average NW diameter was 25nm. The lengths were of the order of tens of microns.

The open regions without NWs constituted about 84% of the surface. The optical transmittance of LED material with AgNWs was about 6% less than without. However, photoluminescence was decreased about 32.5% by having NWs.

The researchers describe the electroluminescence emission as 'strong' in the blue region around 460nm with and without AgNW contact layers. The peak at 20mA was at 457.8nm with AgNWs and at 452.7nm without AgNWs. Increasing the current injection between 10mA and 100mA led to a large shift in wavelength of 3.5nm for the LED without AgNWs. Over the same range, the LED with AgNWs shifted only 0.3nm. The more stable behavior of the device with AgNWs was attributed to better current spreading leading to a decrease in the effective current density through the device.

The researchers comment: "The band-filling effect of the LED without AgNWs appeared to be dominant compared to the LED with AgNWs due to decreased carrier density, resulting in the longer emission wavelength of LEDs with AgNWs than LEDs without AgNWs. Moreover, at increasing injection current, this also likely contributed to the lower blue-shift of LEDs with AgNWs than LEDs without AgNWs."

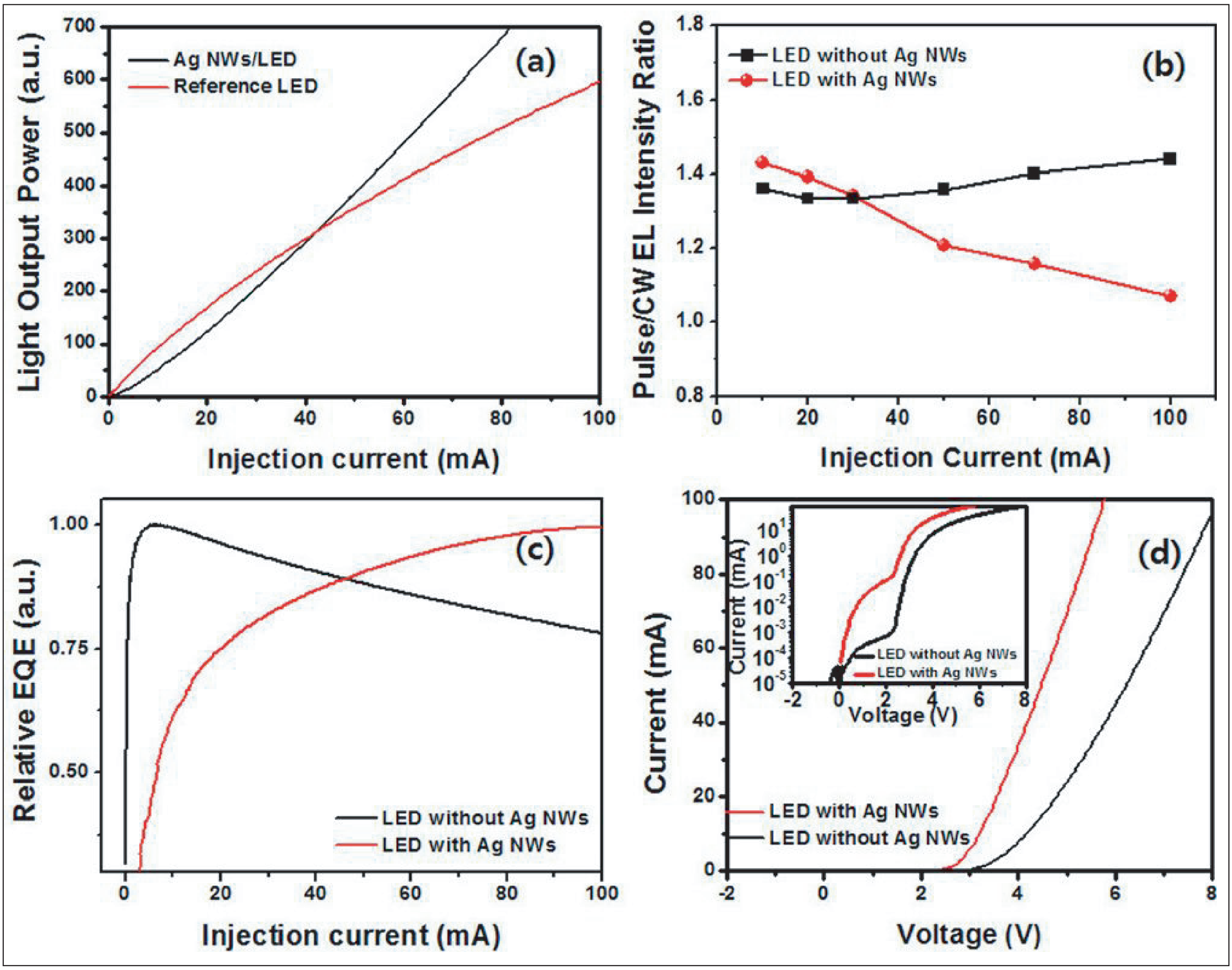

Figure 6. Light output power (a), pulse/continuous wave (cw) EL intensity ratio (b), and relative EQE (c) of GaN-based LEDs without/with AgNWs as a function of injection current. Current–voltage characteristic (d) of LEDs with/without AgNWs.

The spectral line was also narrower for the LED with AgNWs — around 15nm full-width at half maximum (FWHM), compared with ~20nm for the LED without current spreading. Although the FWHM increased in both devices at higher currents, the ~5nm difference was maintained. The researchers attributed the difference to the lower junction temperature (46.8ºC at 50mA, compared with 70.5ºC) in the device with AgNWs.

"We surmised that the narrower FWHMs of the EL spectra originated from a decreasing thermal heating effect due to improved heat dissipation afforded by the AgNWs," the researchers write.

At low injection currents the LED without AgNW current spreading emitted more intense light, but above 45mA the device with AgNWs performed increasingly better (Figure 6). Self-heating effects also adversely affected the light output power of the LED without AgNWs more than for the device with AgNWs. The team comments: "Because AgNWs were effective at dissipating the thermal heat from LEDs, the cw EL intensity of LED without AgNWs was drastically decreased under the high injection current region (>30mA), leading to an increase in the pulse to cw EL intensity ratio."

The EQE of the LED without AgNWs peaked at a very low current, while the efficiency increased over the range up to 100mA for the device with AgNWs. The AgNWs also reduced the turn-on voltage of the diode (2.72V versus 3.22V), also contributing to improved efficiency. Below turn-on the AgNW LED showed a higher series resistance, indicating problems with surface currents. However, above turn-on the series resistance was lower for the AgNW LED. ■

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