

# ZnO mixes it up with nitride semiconductors

**Mike Cooke** reports on recent research that combines ZnO with nitride semiconductors for transparent conduction, light emission and as a substrate.

**Z**inc oxide (ZnO) has potential for conductive coatings, electrodes, substrates and for light emission. It is a low-cost transparent compound semiconductor compared with those containing rare elements such as gallium and indium. Low-cost thin-film transistors using ZnO are a common topic of research, along with nanostructures such as nanowires. ZnO, in ceramic form, is already the basis for varistor components that direct power surges away from sensitive circuitry.

Industry analyst firm NanoMarkets is predicting that the ZnO electronics market could grow more than a factor of three, giving a sales value of \$1.3bn in 2015, and \$2.3bn in 2017. NanoMarkets believes that the market for ZnO LEDs could reach more than \$415m in 2015, while at the same time use as transparent conducting layers (TCLs) could exceed \$220m in 2015.

Here we look at recent research into using ZnO as TCLs, nano-LEDs and substrates.

## TCL for nitride LEDs

For transparent conductive layers (TCLs), ZnO is attractive in cost terms compared with indium tin oxide (ITO), which is widely used for this purpose in displays, LEDs and solar cells to increase the amount of light either leaving or entering the device. In nitride LEDs, thin layers of nickel (Ni) and gold (Au) can be used to create TCLs, but the transparency is rather low at 60–75%.

The desired qualities for a TCL are high transparency and low resistivity: these qualities can be achieved with ZnO films with aluminum, gallium or indium doping. However, ZnO films generally have an n-type character. Unfortunately, there is presently no process available to produce p-type ZnO layers with any measure of stability.

Korean researchers have been developing zinc oxide (ZnO) as a TCL for use with nitride light-emitting diodes (LEDs) with the aim of increasing photon extraction [1]. The researchers come from LED illumination firm Lumimicro Co Ltd, Kyungpook National University, the Korea Photonics Technology Institute, and Pukyong National University.

For use in nitride LEDs one needs the TCL to make ohmic contact (at least approximately) with the p-type gallium nitride (GaN) that is normally the top layer of nitride LEDs. Unfortunately, with n-ZnO on p-GaN one expects a Schottky contact behavior that increases the forward voltage (indicating energy loss/high contact resistance) and also deterioration of performance with temperature.

A further quality needed for the use of doped ZnO as a TCL is a low deposition temperature, since one doesn't want to disturb the previous hard work that has gone into depositing high-quality nitride layers.

It is possible to make ohmic contact between n-ZnO and p-GaN using a thin metal layer, but this requires an undesirable high-temperature anneal step. The Korean researchers preferred to use a silicon-doped (n-type) tunnel junction as an intermediary between the p-GaN and ZnO TCL.

The Al-Ga co-doped ZnO (AGZO) TCL was applied to commercial 2-inch LED epiwafers from Korean supplier Epivalley. The layer structure consisted of undoped GaN (3µm), heavy silicon-doped ( $n^{++}$ ) GaN (2µm), n-GaN (0.5µm), GaN/InGaN multi-quantum well (MQW) active region, magnesium-doped (p) GaN (0.2µm), and a 10nm tunnel junction layer. The tunnel junction consisted of a three-period GaN/In<sub>0.17</sub>Ga<sub>0.83</sub>N structure.

A 300nm AGZO layer was deposited on the epiwafer as TCL using RF sputtering. LED chips were fabricated, along with comparison devices using nickel-gold TCLs. A conventional packaging using epoxy encapsulation was employed.

Before creating the LEDs, experiments were carried out on sapphire to optimize the AGZO deposition process with the aim of low resistivity and high transparency. Sputtering with an argon partial pressure of 1.5mTorr created AGZO films with 96.3% transparency at 460nm wavelengths (blue) and  $6.8 \times 10^{-4} \Omega\text{-cm}$  resistivity (carrier concentration  $4.9 \times 10^{20}/\text{cm}^3$ ).

The AGZO TCLs on the LEDs were characterized with various levels of annealing (Figure 1). Without the anneal, the AGZO-TJ contact was close to ohmic, with a small difference between work functions — i.e.

4.6eV for the AGZO and 4.2eV for the TJ layer. A slight improvement in the ohmic behavior was seen for annealing at 550°C, but Schottky-type behavior occurred at 650°C. The researchers comment that Ga-doped indium oxide ( $\text{In}_2\text{O}_3$ ) and indium tin oxide (solid solution of  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ ) TCLs show similar trends with annealing temperature.

The LEDs produced using an AGZO contact had an increased forward voltage (meaning higher contact resistance) than the Ni/Au comparison devices (Figure 2). For example, at 20mA driving current the forward voltage was 3.84V, which is 0.67V higher than for the Ni/Au LED. The specific contact resistance between AGZO and TJ layers is estimated at  $10^{-2}$ – $10^{-3}\Omega\text{-cm}^2$ . In general, AGZO on GaN has a contact resistance up to two orders of magnitude higher than that of Ni/Au on GaN.

Although the higher resistance of the AGZO contact suggests energy losses, the light output power, with a peak at a wavelength of 453nm, is higher than for the comparison Ni/Au contact. At 20mA, the AGZO LED had an output power of 12.6mW and the Ni/Au LED 7.6mW. These give external quantum efficiencies of 23.0% and 13.9% respectively ( $23.0\% = 1.65 \times 13.9\%$ ). This improvement for the AGZO device is due to the higher transparency of the contact layer: 96.3% rather than 70% for the Ni-Au layer at 460nm.

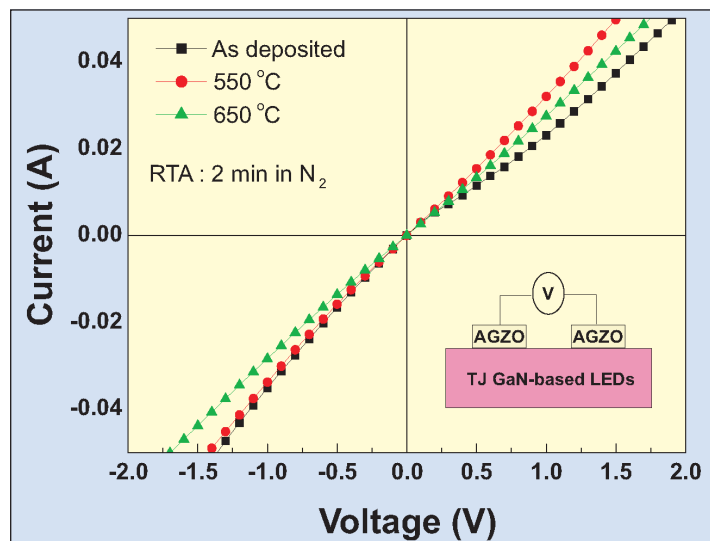
Although the researchers see AGZO thin films as being promising TCLs, leading nitride LEDs without tunnel junction have achieved external quantum efficiencies of more than 60%, so obviously commercial use is going to need more development.

### Nano-wire lights up

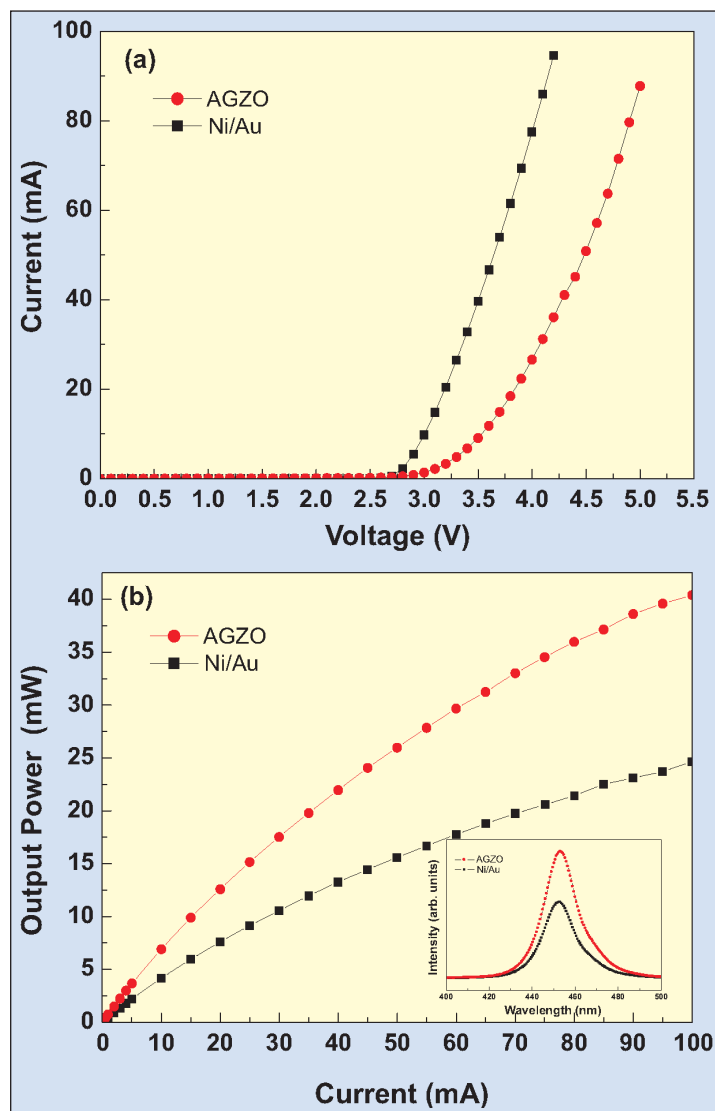
Rather than producing ZnO films, National Institute of Standards and Technology (NIST) researchers Babak Nikoobakht and Andrew Herzing have developed ZnO nanowires on p-GaN substrates to yield 'nano-LEDs' [2].

The nanowires are grown at 900°C using solid-vapor-liquid-solid deposition in a tube furnace with a gold catalyst previously deposited and patterned on the GaN substrate. The GaN substrate was a commercial product (from TDI) with p-type magnesium doping ( $\text{Mg}$  concentration  $\sim 5 \times 10^{17}/\text{cm}^3$ ). The zinc source comes from a ZnO-graphite mixture placed on a silicon substrate. Ultra-dry nitrogen is used as a carrier gas.

Unlike many ZnO nanowire growth methods, NIST creates ZnO nanowires in the plane of the GaN substrate, rather than perpendicular/vertical forests of nanowires. As the NIST ZnO wire grows it pushes the gold nanoparticle along the GaN surface. The direction of growth depends on the crystal structure of the substrate and also on the direction of flow of the carrier gas — the growth tends to be into the wind. Further control of the growth direction can be achieved by laying down lines of gold to block growth in particular directions. ➤

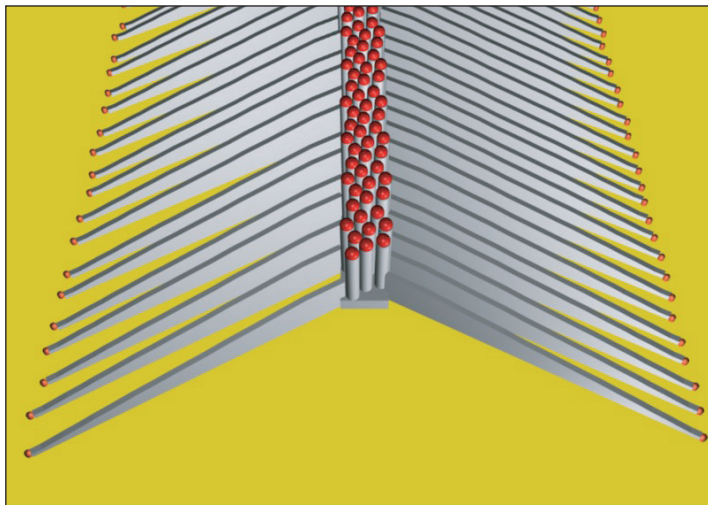


**Figure 1.** Current-voltage characteristics of TJ GaN-based LEDs with AGZO transparent conducting layer as a function of annealing temperature. Inset shows schematic configuration for measurement.

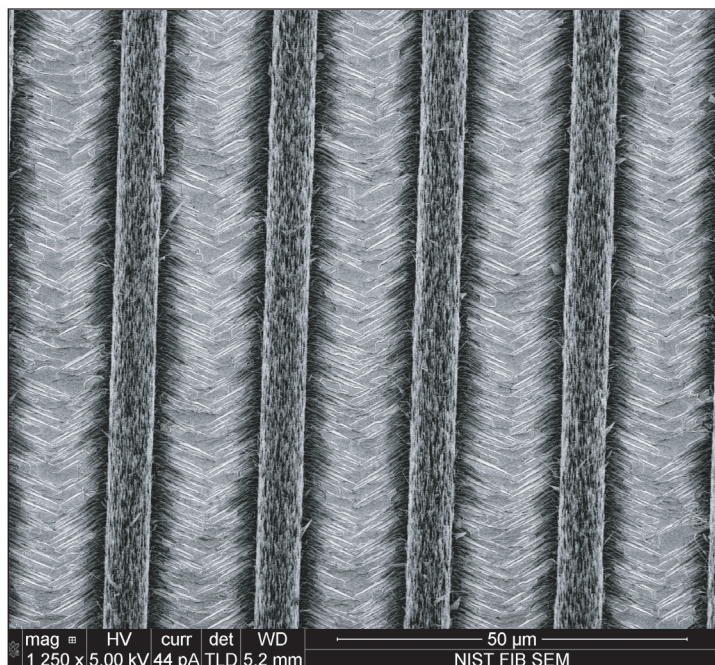


**Figure 2.** Comparisons of AGZO (300nm) and Ni/Au (5/5nm) TCLs: (a) current-voltage, (b) light output power vs current, and (inset) emission spectra.

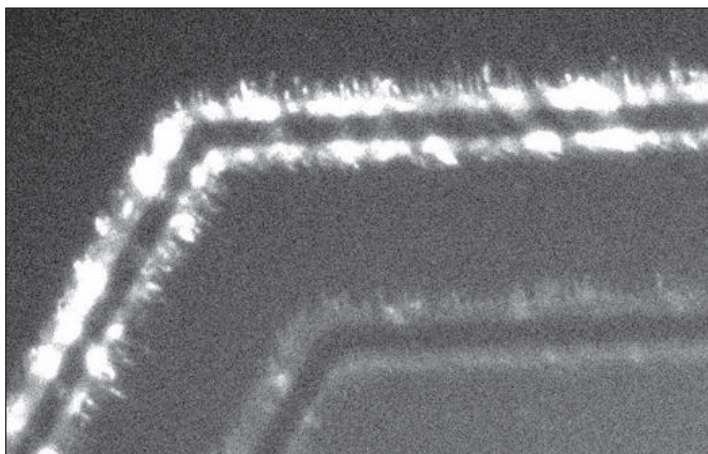




**Figure 3. Single row of nanowires (cylinders with red tops) with fin-shaped nanowalls extending outward.**



**Figure 4. Transmission electron micrograph (TEM) shows four rows of nanowires and their corresponding nanowalls. The distance across the micrograph is approximately the diameter of a human hair.**



**Figure 5. TEM image of nano LEDs emitting light.**

In previous work, NIST researchers used an 8nm nanoparticle catalyst. In the new research, they increased the nanoparticle size to 20nm for some of their experiments. This resulted in wires that grew secondary shark-like 'dorsal fins' or 'nano-walls' (Figures 3 and 4). The height of the nano-wall gradually decreases as one goes toward the leading edge where the nano-particle is. This suggests that the further growth is due to a slower self-catalytic process on the wire created by the nano-particle.

The ZnO material in these structures has an n-type conduction characteristic with an electron density of  $\sim 10^{18}/\text{cm}^3$ . The individual heterojunctions measure about 10μm long and 80nm wide. Various characterizations were performed — such as selected-area diffraction (SAD) and x-ray energy-dispersive spectroscopic (XEDS) imaging — that suggested that the junction between the ZnO and GaN crystal structures was abrupt.

When charge crossed the p-n GaN-ZnO junction, light was emitted (Figure 5). The current was injected with titanium-gold electrodes for the n-ZnO contact and nickel-gold for the p-GaN contact. Under forward bias the emission was around the violet 390nm (3.18eV) wavelength (32nm full-width half-maximum) that is related by the researchers to the ZnO exciton (electron-hole bound state with a binding energy  $\sim 60\text{meV}$ ). The strong exciton emission would suggest that most of the forward bias recombination occurred in the ZnO crystal structure with holes being injected from the underlying p-GaN.

Light was also emitted under reverse bias — around an orange wavelength of 640nm (1.95eV). The intensity of the radiation reduced in smaller devices with better rectifying behavior and higher breakdown voltage (9V rather than 4V). The researchers suggest that this emission could result from a transition between an intrinsic shallow state to a deep state such as those associated with oxygen vacancies. The researchers say that the reverse bias emission is 'still under study'.

Nikoobakht and Herzing hope to improve the nano-LEDs in future by using better geometries and material design. The researchers want to apply the devices in a number of contexts, giving light sources and detectors for photonic devices or lab-on-a-chip microsystem platforms. These devices could be powered by nano-generators. For example, zinc oxide is commonly used in prototype nano-generator systems that depend on vibration, since it has a powerful piezoelectric effect (strain-dependent polarization electric field). Meanwhile, nitride semiconductors are being developed by some as solar cell materials. The researchers suggest similar techniques could be used to grown ZnO nano-structures on other nitrides such as indium gallium nitride or aluminum gallium nitride.

## ► Multi-emissions from nitride on ZnO

Rather than depositing ZnO on GaN, earlier this year researchers reported for the first time growth of p-type nitride semiconductor layers on ZnO substrates, enabling the creation of two sets of diode devices with light emission at two wavelengths (near-UV and yellow, green and blue) [3]. The researchers came from Virginia's Old Dominion University (ODU), Georgia Institute of Technology (GaTech),

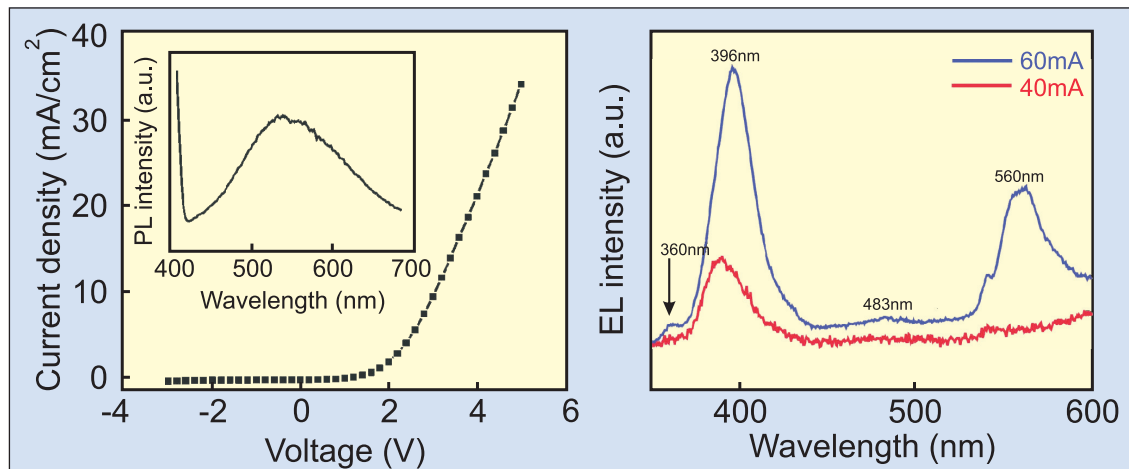
State University of New York at Buffalo, Korea University and substrate maker Cermet Inc of Atlanta, GA, USA.

Theoretically ZnO is an attractive substrate for growing nitride semiconductors. The c-axis mismatch to GaN is only 0.4% and the a-axis mismatch is 1.9%. By contrast, the lattice mismatch for GaN/sapphire growth is about 14%. Large-diameter ZnO wafers can be prepared at relatively low cost using hydrothermal growth.

Unfortunately standard nitride semiconductor growth techniques such as metal-organic chemical vapor deposition (MOCVD) or even molecular beam epitaxy (MBE) are difficult to use with ZnO substrates. Previous attempts to grow p-type semiconducting nitrides have foundered on the volatility of ZnO and compensation of the p-type conduction in GaN by oxygen migration into the nitride layers.

Namkoong et al used low-temperature (500–550°C) molecular beam epitaxy (MBE) to grow nitrides on Zn-face ZnO substrates produced by Cermet. A 50nm layer of  $\text{In}_{0.07}\text{Ga}_{0.93}\text{N}$  was followed by 0.4 $\mu\text{m}$  of p-GaN (Mg-doped to hole concentrations of  $3\text{--}5 \times 10^{17}/\text{cm}^3$ ). Both layers were produced using 'metal-rich' conditions. The substrate, as delivered, had an electron concentration of  $3 \times 10^{16}/\text{cm}^3$ . A comparison nitride semiconductor LED on sapphire was also produced with 0.15 $\mu\text{m}$  Mg-doped p-GaN ( $3 \times 10^{17}$  holes/ $\text{cm}^3$ ) on 1 $\mu\text{m}$  silicon-doped n-GaN ( $1 \times 10^{18}$  electrons/ $\text{cm}^3$ ).

Photoluminescence (PL) and electroluminescence (EL) studies were carried out. First electronic characterization of the diode properties showed increased ( $\sim 4\times$ ) forward current for given voltage, comparing the nitride-on-ZnO device with a nitride-on-sapphire arrangement. However, blocking of reverse current was not as good in the hybrid III-N/ZnO device. The forward current is enhanced with the ZnO substrate



**Figure 6. I–V characteristic (a) and EL spectra (b) of p-GaN/InGaN/n-ZnO with different forward currents. Inset of (a) shows photoluminescence of p-type GaN/InGaN/ZnO structures measured at room temperature. The peaks at higher current are attributed to emissions from the GaN band edge (360nm), InGaN band-edge (396nm), Mg-related defects (560nm), Zn deep-acceptors in InGaN (483nm).**

both by its greater electrical and thermal conductivities. Sapphire is insulating and has poor thermal conductivity.

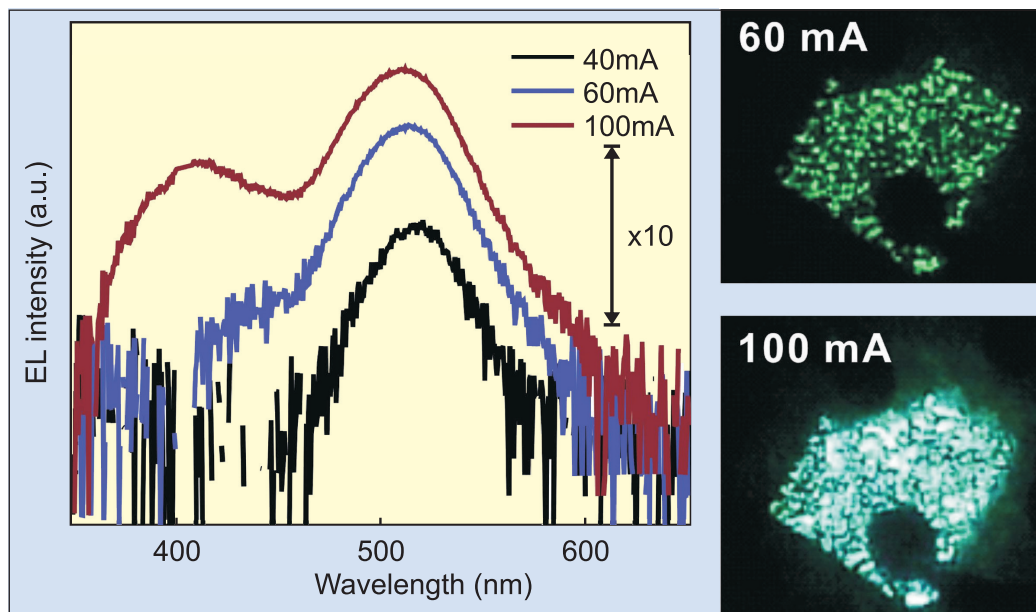
The EL spectra of the hybrid ZnO/nitride LEDs show two main peaks (Figure 6) at high currents (60mA): one at 396nm (near-UV); the other at 500nm (yellow). A weak peak at 483nm (blue) is also observed. Energy dispersive spectroscopy (EDS) suggested that the blue peak was due to inter-diffusion at the InGaN/ZnO interface, in particular deep acceptor states from Zn that had migrated into the InGaN layer. The near-UV is attributed to band-edge emission of the InGaN material. There is also band-edge emission in the GaN layer at 360nm.

Further devices were grown with higher indium content ( $\text{In}_{0.14}\text{Ga}_{0.86}$ ) that gave blue and green emissions (Figure 7). The 516nm green emission was dominant at 40mA. The green emission was attributed to Zn-related band emission in the InGaN layer. At 60mA and 100mA, a shorter wavelength peak appears that blue-shifts from  $\sim 432\text{nm}$  (2.87eV) to 411nm (3.01eV) with increasing current. Non-optimal growth conditions are a likely source of non-uniformities of the emissions seen in Figure 7(b).

The researchers concluded that "multi-quantum well (MQW) structures in the active layer may produce bright dual wavelengths if impurities from the ZnO diffusing into the InGaN active layer are carefully controlled".

Further work would involve reducing dislocation densities, increasing hole conductivity, and controlling interfaces between III-nitride and ZnO substrates. This could enable brighter dual- or even triple-wavelength devices, if combined with MQW structures. Gon Namkoong, the corresponding author on the research, based at ODU, reported that work had been carried out on phosphor-free white LED emissions. ►





**Figure 7. EL spectra (a) of p-GaN/In<sub>0.14</sub>Ga<sub>0.86</sub>N/ZnO LEDs and photographs (b) of LEDs at different forward currents. In (a), intensity scale is logarithmic.**

### ► r-GaN on ZnO

Another area where ZnO substrates may come in handy is for producing green laser diodes. In producing LEDs and laser diodes (LDs), many groups are working to eliminate, or at least mitigate the quantum-confined Stark effect (QCSE). In GaN MQWs there are high electric polarization fields in the material due to strain (piezoelectric) of the mismatched lattices of the well/barrier layers. These fields shift the electron and hole energy bands, but worse they tend to separate the oppositely charged carriers, reducing their ability to recombine into a photon.

These effects are at their worst in c-plane nitride semiconductors — the standard growth direction in commercial production. In the past few years, substrates that allow growth of structures with different nitride crystal orientations have become available. These structures have enabled longer wavelength (green) LDs and more efficient LEDs. Green LDs have been produced by Sumitomo using {20 $\bar{2}$ 1} plane substrates. However, it has been predicted that the most effective devices would be produced on substrates where the growth direction is around 45° to the c-direction. This angle is close to that of the r-plane {1 $\bar{1}$ 02}.

Such r-plane films have been grown on ZnO substrates using pulsed laser deposition (PLD) by researchers at University of Tokyo's Institute of Industrial Science and Japan Science and Technology Agency's CREST organization [4]. PLD is used because ZnO is not an ideal substrate medium for nitride growth using either MOCVD or MBE because the process conditions used tend to attack the substrate.

The ZnO substrates were subjected to chemo-mechanical polishing (CMP) and annealing in air at 1250°C for 3.5 hours inside a box made of ZnO.

Degreasing in ethanol was carried out for 10 minutes. Once in the PLD vacuum chamber, a further 800°C anneal was carried out for 30 minutes. GaN layers were deposited at room temperature to create a buffer. The deposition temperature was then increased to 700°C. The laser deposition consisted of ablating liquid gallium with a krypton-fluoride excimer laser (248nm, 20ns pulse) and depositing on a substrate 5cm away. PLD is hence a variation on physical vapor deposition. The nitrogen source consisted of RF plasma generated radicals.

Various characterizations were carried out: reflection high-energy electron diffraction (RHEED),

atomic force microscopy (AFM), high-resolution x-ray diffraction (XRD), and low-temperature (15K) photoluminescence (PL). It was found that 1μm GaN films

**Peaks that have been related by other groups to prismatic stacking faults or partial dislocations were reduced in films on ZnO substrates that had been annealed in the ZnO box. The PL peak at 3.44eV at room temperature is indicative that Zn diffusion into the main GaN layer is blocked by the buffer layer**

produced on ZnO substrates that had been prepared using both CMP and annealing in the ZnO box had 5x the PL response due to near-band-edge emission compared with films on ZnO substrates just subjected to CMP.

Also, the strength of peaks that have been related by other groups to prismatic stacking faults (PSFs) or partial dislocations (PDs) were reduced in films on ZnO substrates that had been annealed in the ZnO box. The researchers also believe their PL peak at

3.44eV at room temperature indicates that Zn diffusion into the main GaN layer is blocked by the buffer layer. ■

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

### References

1. Tae Hoon Kim et al, Jpn. J. Appl. Phys., vol49, p091002, 2010
2. Babak Nikoobakht and Andrew Herzing, ACS Nano, published online 15 September 2010
3. Gon Namkoong et al, Appl. Phys. Express, vol3, p022101, 2010
4. Atsushi Kobayashi et al, Jpn. J. Appl. Phys., vol49, p100202, 2010

# Advances in p doping and polarity control for GaN and ZnO

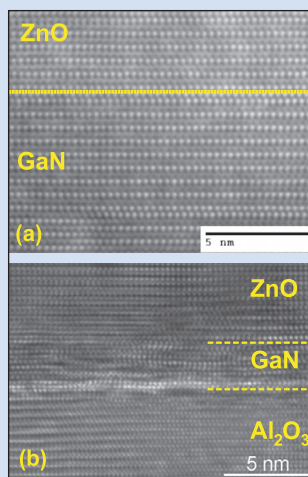
Creating holes is a problem for both GaN and ZnO. However, in nitride semiconductors a workable solution was developed, creating the nitride semiconductor industry from the 1990s up to the present day. The magnesium doping used in GaN is not ideal and forms one of the road-blocks to higher-efficiency devices. Hydrogen is implicated in passivation of the Mg doping, limiting hole concentrations to less than  $10^{18}/\text{cm}^3$ . There are a number of theories on why p-ZnO is so difficult to realize, including a hydrogen-based concept.

A nickel film deposited on top of p-GaN can be used as a catalyst to desorb hydrogen from p-GaN material, but in thermal treatments above 600°C it has a nasty tendency to also desorb nitrogen, leaving vacancies in the nitride crystal structure that reduce the hole concentration.

Chinese Academy of Sciences' Semiconductor Lighting Technology Research and Development Center has also looked at alternative hydrogen desorption catalysts — namely platinum and molybdenum [Tongbo Wei et al, Jpn. J. Appl. Phys., vol49, p100201, 2010]. The metal films were deposited on p-GaN layers with Mg concentration  $\sim 10^{20}/\text{cm}^3$ . The doping was then activated in a quartz tube furnace in nitrogen for 15 minutes at 720°C. These metals resulted in higher hole concentrations ( $\sim 5 \times 10^{17}/\text{cm}^3$ ) compared with p-GaN layers without treatment ( $\sim 2 \times 10^{17}/\text{cm}^3$ ) or with a nickel catalyst ( $\sim 3 \times 10^{17}/\text{cm}^3$ ). However, platinum resulted in better ohmic properties than the other options (see Table).

For ZnO, a team coming from China's 'Key Laboratories' for 'Superhard Material' and 'Excited State Processes' claim to have produced single wurtzite p-type  $\text{Zn}_{1-y}\text{Cu}_y\text{O}_{1-x}\text{S}_x$  alloy films ( $0.081 < x < 0.186$  and  $0.09 < y < 0.159$ ) with 'very stable' p-type conductivity with hole concentrations in the range  $4.31\text{--}5.78 \times 10^{19}/\text{cm}^3$ , a resistivity of  $0.29\text{--}0.34 \Omega\text{cm}$  and a mobility of  $0.32\text{--}0.49 \text{cm}^2/\text{Vs}$  [H. L. Pan et al, Appl. Phys. Lett., vol97, p142101, 2010]. The deposition process was magnetron sputtering on quartz.

These researchers believe the p-type conductivity to a  $\text{Cu}^{+1}$  substitution at a Zn site, creating an acceptor state with an ionization energy of 53meV. They comment that this is much less than for Cu-doping of ZnO. The small energy is thought to result from the heavy Cu-doping and the lifting of the valence band maximum induced from the alloying with S.



**HRTEM images of ZnO/20nm-GaN (a), ZnO/3nm-GaN (b) around interface between ZnO and GaN.**

Control of the polarity of ZnO layers grown on GaN can be important. For example, the incorporation and doping efficiency of nitrogen for creating p-type ZnO is affected by the polarity of the crystal structure.

Researchers at China's State Key Laboratory of Artificial Microstructure and Mesoscopic Physics (Peking University) and University of Michigan in the USA have studied ZnO layers grown on sapphire with a GaN interlayer [X. Q. Wang et al, Appl. Phys. Lett., vol97, p151908, 2010]. Samples were grown using RF-plasma-assisted molecular

beam epitaxy performed at Japan's Chiba University.

Using coaxial impact collision ion scattering spectroscopy (CAICISS), these researchers found that 3nm GaN interlayers produced Zn-polar ZnO, while thicker (20nm), better quality interlayers resulted in O-polar material. It is thought that these results are due to Zn-polar ZnO being more stable on an amorphous interface where some O atoms replace N in the GaN structure. For the thicker interlayer, where the interface is much smoother, the ZnO growth follows that of the underlying GaN, leading to O-polarity.

The MBE process was preceded by a nitridation process where the sapphire substrate was exposed to nitrogen plasma at 400°C for two hours, forming a thin AlN layer with N-polarity. This step thus tends to create GaN layers also with N-polarity, as opposed to the Ga-polarity that is usual in MOCVD-grown nitrides. (MOCVD-grown ZnO tends to show Zn-polarity.)

The researchers believe that these results could be the basis for a useful method to create ZnO layers with given polarity. They comment: 'The advantage of this

method is the following: (1) the polarity of ZnO is well controlled by modifying the growth parameters of the GaN layer; and (2) the quality of ZnO can be improved due to the same lattice structure and small lattice mismatch between ZnO and GaN.'

**Hall-effect results of Mg-doped GaN films activated without and with metal catalytic films at 720°C.**

p-GaN condition	Resistivity ( $\Omega\text{cm}$ )	Hole concn ( $10^{17}/\text{cm}^3$ )	Hole mobility ( $\text{cm}^2/\text{Vs}$ )	Specific contact resistance ( $10^{-2}\Omega\text{cm}^2$ )
No metal	1.77	2.2	26.1	12.2
With Ni	0.75	3.4	23.2	8.2
With Pt	0.48	5.3	23.6	2.9
With Mo	0.46	5.1	24.8	13.6