Bridging the amber-green gap and white LEDs

Mike Cooke reports on recent reports of various techniques to create light-emitting diodes that could fill the chasm, possibly leading to whiter LEDs.

Presently, standard commercial white light LEDs use phosphor layers to convert short-wavelength light from indium gallium nitride (InGaN) LEDs into something that the eye will see as being an approximation to 'white'. Phosphors make the production process more complicated and costly. Lower-cost devices with phosphors have poor color rendering. Technical difficulties include reliability problems, and degraded color balance over time and due to temperature stress.

A preferable solution, if it can be made economic, would be to combine light from four LEDs with different wavelength properties. A suggested combination of wavelengths is 459nm (blue), 535nm (green), 573nm (yellow/'amber'), and 614nm (orange). The blue and orange targets are well covered by existing technology.

Production of LEDs with yellow (590–560nm) or green (560–490nm) emission is presently difficult commercially. The long- and short-wavelength ends of the visible spectrum are covered using phosphide and nitride semiconductor materials, respectively.

The nitride semiconductor approach to longer wavelengths involves problems such as enhanced efficiency droop and difficulties in growing high-quality InGaN with high indium content.

From the non-nitride III-V semiconductors, the material with widest bandgap is aluminium indium phosphide (AlInP). However, this option has not been researched extensively due to a lack of a convenient substrate and uncertainties about the material system's characteristics, such as the region of aluminium concentration for which the gap is 'direct' and where light can be efficiently produced from electron–hole recombination.

Quantum well engineering

Chinese Academy of Sciences' Semiconductor Lighting R&D Center at the Institute of Semiconductors in Beijing has developed an electrically driven color-tunable LED based on InGaN quantum wells in gallium nitride (GaN) barriers [Hongjian Li et al, Appl. Phys. Express, vol6, p102103, 2013]. At high current injection, the devices achieve a white color rendering index of 85.6 — much higher than for conventional yellow-phosphor-converted 'white' LEDs. At the low-current end, the devices emit red light around 630nm.

The color-tunability arises from the nitride semiconductor growth process rather than from complicated device structures or fabrication methods such as

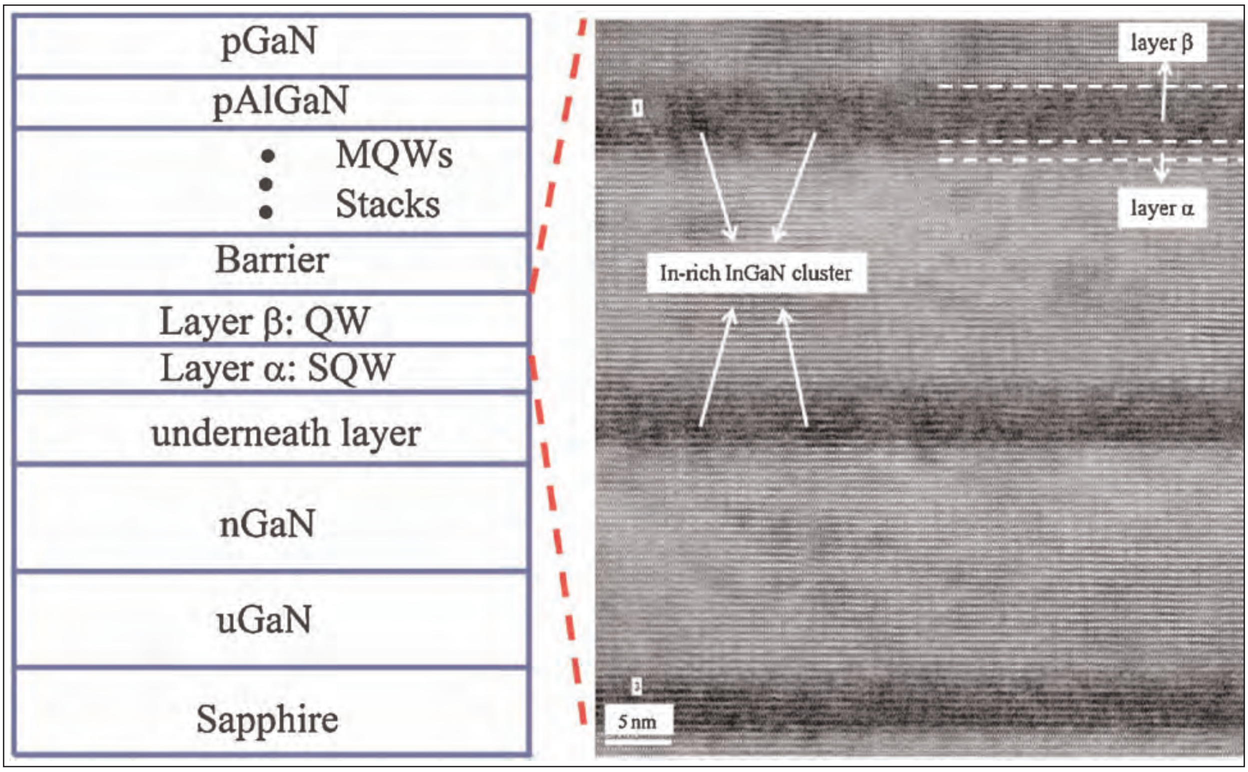

Figure 1. Epitaxial structure, left, and HRTEM image of active region, right.

adding phosphor layers. The researchers see their development as providing "a simple method for the fabrication of phosphor-free color-tunable monolithic LEDs and also an alternative for high-color-quality general lighting".

The nitride semiconductor layers (Figure 1) were grown on c-plane sapphire using metal-organic chemical vapor deposition (MOCVD). The quantum wells consisted of a combination of low-indium-content (13%, layer α) InGaN 1nm shallow wells (SQW) and deeper high-indium-content (46%, layer β) InGaN 3nm wells. Barriers between the wells were 17nm pure GaN. Growth of the α layer before the main β well improved crystal quality, served as a carrier reservoir, and enabled shorter-wavelength emissions.

High-resolution transmission electron micrographic (HRTEM) study showed indium-rich InGaN clusters of 2–4nm diameter embedded in the deep quantum well regions. The researchers attribute the clusters to strong indium phase separation and composition fluctuations due to the large biaxial strain from the large lattice mismatch between InN and GaN (11%). The indium-rich clusters in high-indium-content InGaN result in deep localization centers for carrier recombination. Clusters are a common feature of high-indium-content (more than 20% In) InGaN.

Photoluminescence showed peaks at 2.12eV (P1) and 2.91eV (P2). The P1 peak is attributed to the shallow well, while P2 correlates with the deep well with localized centers. Temperature-dependent measurements suggested internal quantum efficiencies of 10.4% and 14.1% for P1 and P2, respectively.

Standard mesa-type LEDs of 500μm x 1000μm size were produced with indium tin oxide (ITO) transparent conductor current spreader on the p-contact layer. The contact electrodes were chromium/platinum/gold.

The spectral content of electroluminescence (EL) emission shifted significantly with increasing current from red (5mA) through yellow (10–20mA) to 'white' (100mA). The turn-on voltage of the device was 2V and the forward voltage at 100mA was 3.06V.

The spectra of the emissions showed a dominant red (631nm) peak at 5mA. This peak blue-shifted to 615nm and 608nm at 10mA and 20mA, respectively. The width of the peak broadens from a full-width at half-maximum (FWHM) of 185meV at 5mA to 274meV at 60mA. The broadening is attributed to filling of the deeper localization states as the current increases that allows shallower localization states to become active. Above 60mA, a second peak appears at 473nm, attributed to the shallow well.

The researchers plotted Commission Internationale de l'Éclairage (CIE) chromaticity coordinates and determined the color temperature at the various currents (Figure 2). The color rendering index (CRI) at 250mA was 85.6.

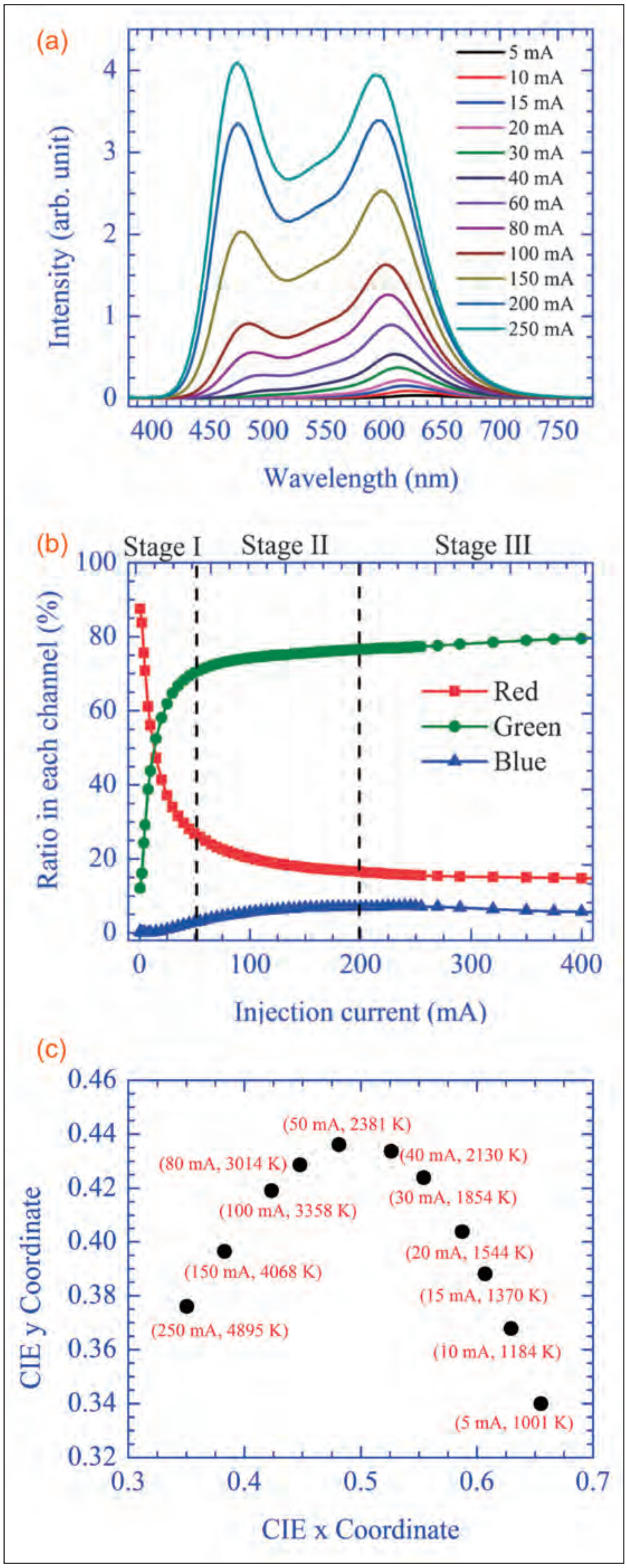

Figure 2. (a) EL spectra at various injection currents. (b) Intensity ratio in red/green/blue channels versus injection current. (c) CIE chromaticity coordinates at various injection currents.

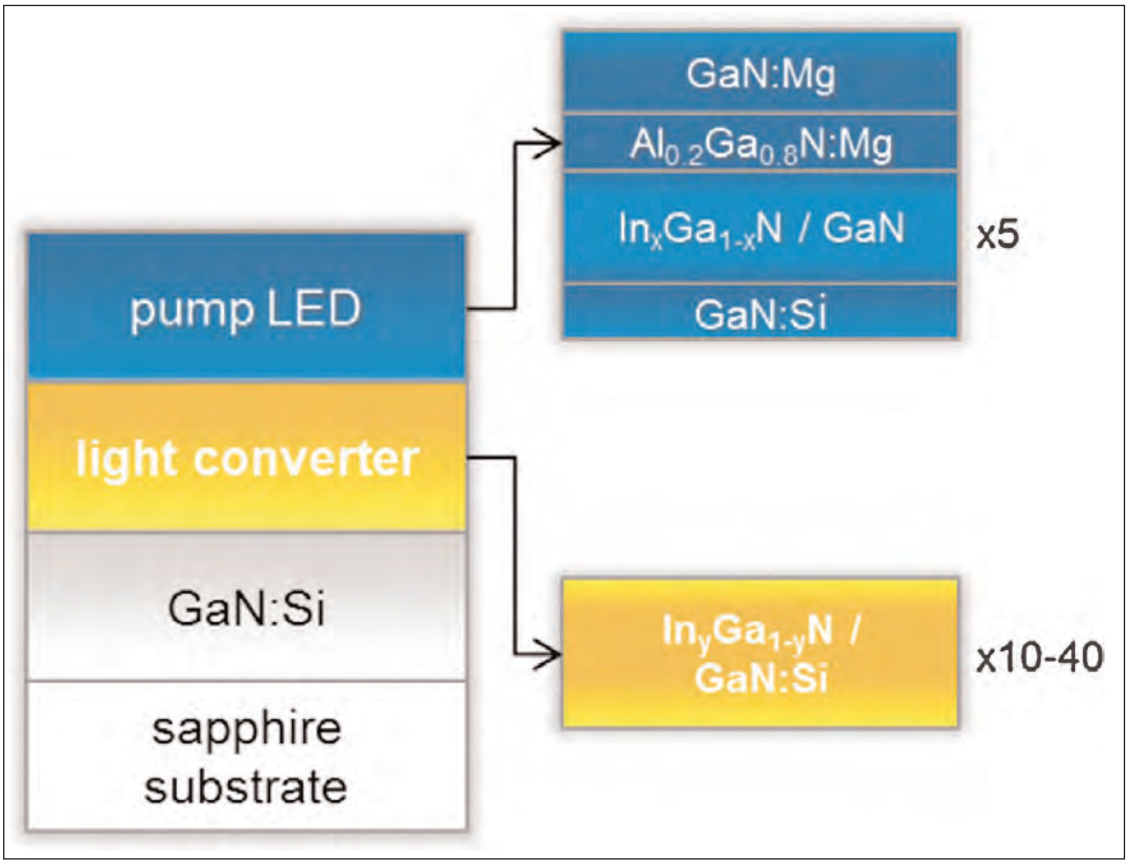

Figure 3. Structure of monolithic LED with light converter.

Monolithic pump / light conversion

Researchers in France have developed a monolithic metal-organic chemical vapor phase epitaxy (MOVPE) process for growing indium gallium nitride (InGaN) LEDs with a multiple quantum well (MQW) light converter as an alternative to phosphors [Benjamin Damilano et al, Appl. Phys. Express, vol6, p092105, 2013]. The research involved Centre de Recherche sur l'Hétéro-Epitaxie et ses Applications–Centre National de la Recherche Scientifique (CRHEA-CNRS) and University of Nice Sophia-Antipolis.

The short-wavelength LED region was used as a pump for photoluminescence from an InGaN MQW structure that emits longer wavelengths. The researchers have previously developed such structures with a production process using molecular beam epitaxy (MBE), sometimes in combination with MOVPE. Commercial production of InGaN LEDs is usually based on MOVPE.

A problem with MOVPE is that it uses higher growth temperatures than MBE that can degrade high-indium-content InGaN needed for longer wavelengths.

The researchers developed an MOVPE process that uses a lower temperature, but does not degrade the pump LED performance.

The nitride semiconductor layers (Figure 3) were grown on commercial n-type silicon-doped GaN on sapphire using MOVPE. First, a 0.5μm layer of GaN:Si was grown at 1080ºC. The temperature was reduced to 715–780ºC for the $In_yGa_{1-y}N$ layers in the light conversion MQW.

The researchers found that they were able to produce light conversion from violet into blue to red (490–605nm). Although spectral purity is often desired in colored LEDs, for white light sources with good CRIs, the researchers wanted broad photoluminescence peaks. Such broadening can occur due to fluctuations in the InGaN alloy composition or from QW interface roughness.

Four pump/converter structures were produced with varying light converter regions (Table 1). The InGaN of the pump MQW was grown at 800ºC.

The standard growth temperature for GaN and AlGaN of ~1080ºC was found to result in poor performance. In particular, the light converter regions showed signs of indium metal clustering. Thus, a lower temperature of 970ºC was adopted while, at the same time, the p-doping effect of magnesium (Mg) had to be re-optimized for the lower growth temperature.

The samples were used to produce on-wafer LEDs by scratching the top surface with a diamond tip, exposing the GaN:Si layer of the pump LED. The electrical contacts with the GaN:Si and GaN:Mg layers were made with indium metal.

Despite the non-standard growth, the researchers were able to produce violet LEDs with ~2mW output power at 20mA, similar to values obtained for devices grown at higher temperatures. The peak of the pump's emission spectrum was around 400nm.

The effect of the light converters (Figure 4) was to add peaks at 490nm (sample A), 526nm (B), 551nm (C), and 605nm (D). The researchers describe these devices as emitting blue, green, yellow-green, and white-orange light, respectively.

Table 1. Structures of various light converter sections.

Sample	A	B	C	D
Number of QWs	20	10	40	40
$In_yGa_{1-y}N$ thickness (nm)	1.6	3.4	3.1	3.1
In composition (y)	0.26	0.18	0.22	0.28
GaN:Si barrier thickness (nm)	21	18	18	18

The fractions of the long-wavelength peak relative to the total electroluminescence intensity were, in order, 60%, 55%, 70% and 43%. Despite the expected degradation in performance from increased indium content, sample C shows an increased fraction of the longer-wavelength peak. The researchers ascribe this to greater absorption from the use of 40 quantum wells rather than the 10 of sample B.

The 50mA luminous powers for samples A–D were 86mlm, 264mlm, 67mlm, and 5mlm, respectively. Since lumens corrects for the eye's sensitivity to light of different wavelengths with a maximum in the green part of the spectrum (683lm/W at 555nm), the optimum luminous power is for sample B. Previous attempts to use a pump/light converter structure have produced 200mlm for material grown using a mix of MOVPE (converter) and MBE (pump). Sample B beats this previous achievement by 32%.

In terms of chromatic coordinates, sample D is near that of a blackbody of temperature 2100K. This tint is between warm white and candlelight.

The researchers believe the work could be extended to include a range of emissions from the converter section. This could be used to improve the CRI to bring it more in line with a white light source at various color temperatures.

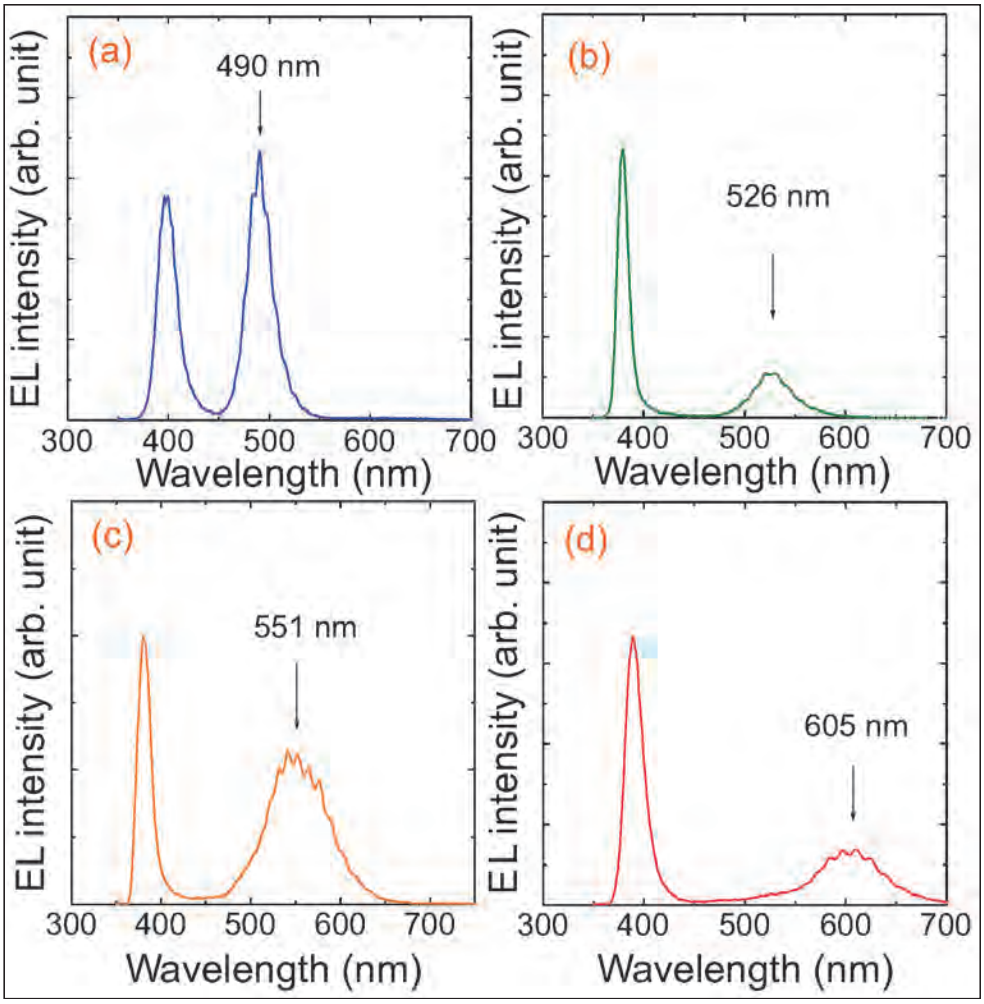

Figure 4. (a)–(d) RT EL spectra under continuous wave conditions at a current of 20mA corresponding to samples A–D.

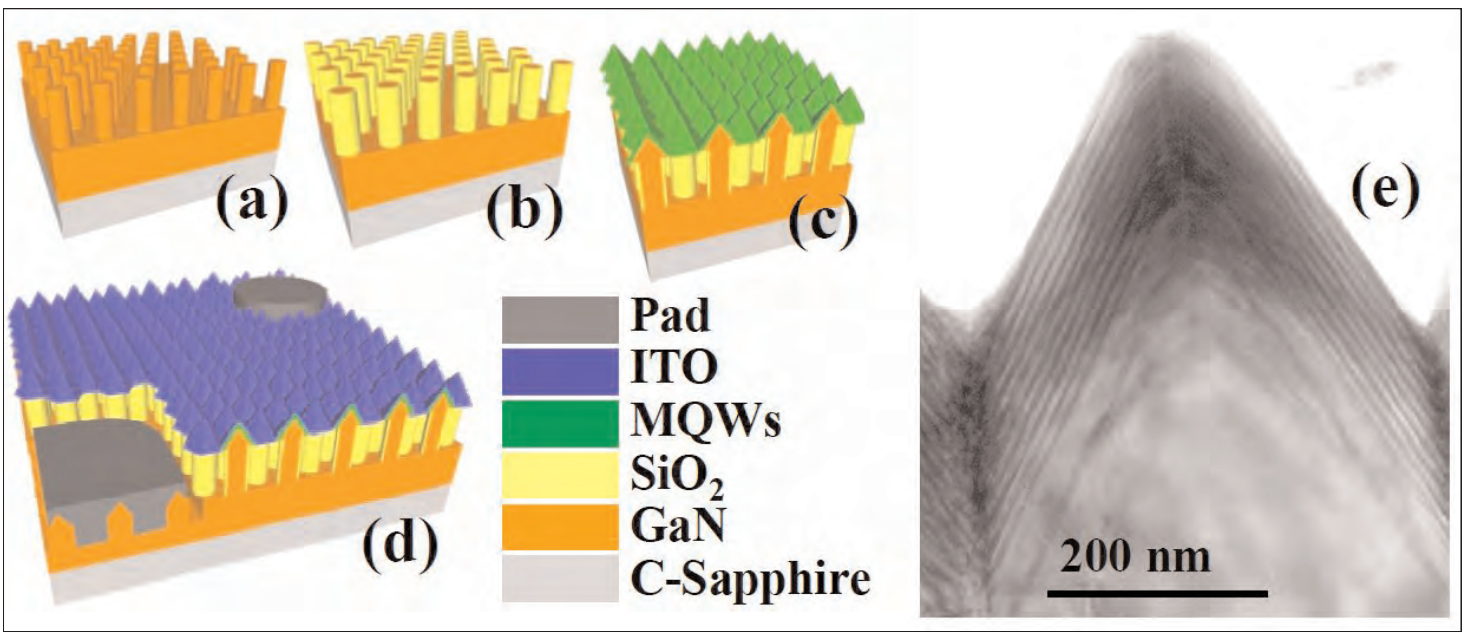

Figure 5. Nanopyramid LED fabrication: (a) Patterned top-down etch of nanopillars. (b) Sidewall coated with oxide. (c) Nanopyramid followed by MQW growth. (d) Top surface ITO deposition and metal pad fabrication. (e) HRTEM cross-section from sample after MQW growth.

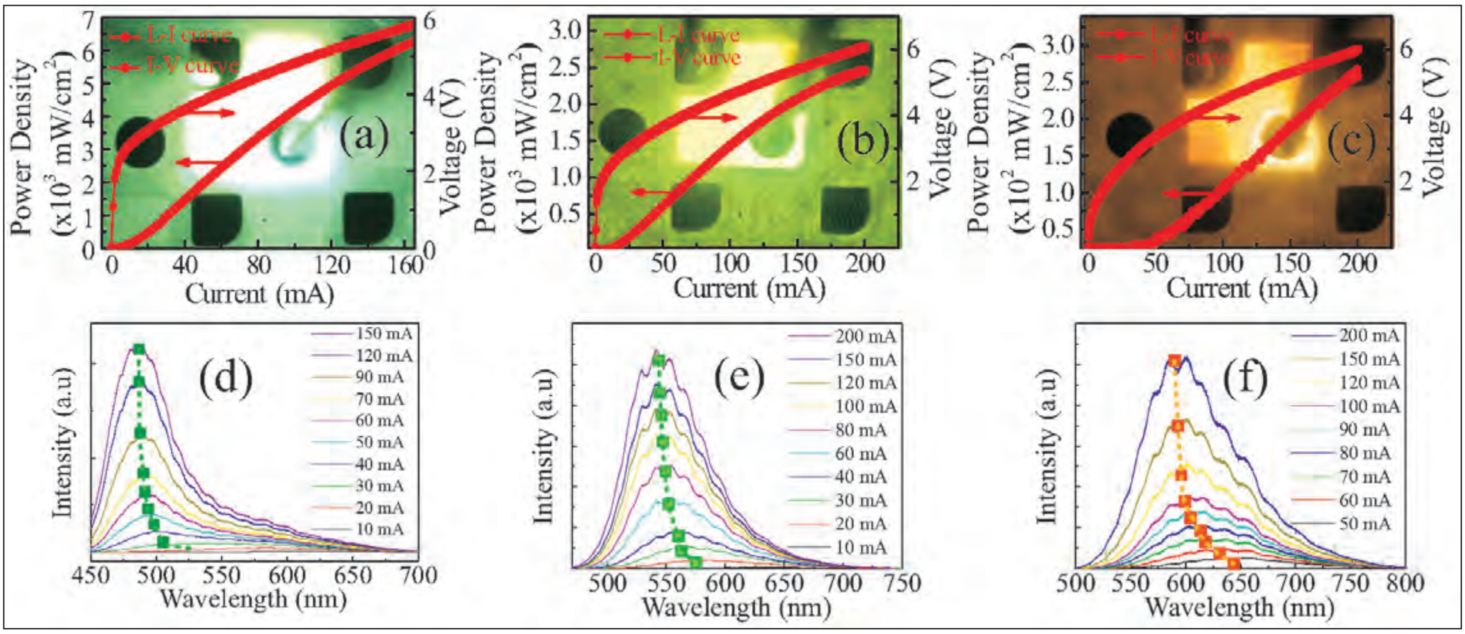

Figure 6. (a)-(c) Optical microscope images of G-, O-, and A-LED under electrical injection. (d)–(f) Electroluminescence spectra versus injection current.

Nanopyramids

Researchers in Taiwan have used nanopyramid nitride semiconductor structures to create long-wavelength green, olivine and amber LED structures [Shih-Pang Chang, Optics Express, Vol. 21, p23030, 2013].

The team was variously based at National Chiao Tung University and Academia Sinica's Research Center for Applied Sciences. The researchers also used technical expertise from Epistar Corp, LuxtalTek Corp and Industrial Technology Research Institute (ITRI), all similarly based in Taiwan.

The device performances compared favorably with LEDs produced on c-plane sapphire. It is thought that producing the light-emitting structures on the semi-polar facets of hexagonal GaN nano-pyramids reduces the spontaneous and strain-dependent (piezo-) electric fields that arise in indium gallium nitride (InGaN) quantum wells. These fields in polar c-plane devices keep the electrons and holes from recombining into photons, reducing efficiency.

Although semi-polar and even non-polar substrates can be produced, they are not readily available.

The fabrication process (Figure 5) began with an n-GaN template on sapphire. First, nanocolumns were formed in a patterned etch. The column sidewalls were coated with spin-on glass (SiO_2). The GaN semiconductor nanopyramids, with additional InGaN/GaN nitride (2nm/8nm) MQWs and p-GaN top contact, were grown by MOCVD on the tops of the nanocolumns. The spin-on-glass coating was aimed at blocking regrowth of nitride semiconductor on the sidewalls of the columns.

Further processing included applying an ITO transparent top contact and mesa etching to reach the n-GaN contact layer to create 300μm x 300μm LEDs. Three different emission types were produced by varying the indium content of the InGaN wells. The peak wavelengths at 100mA were 500nm (green/G), 550nm (olivine/O), and 600nm (amber/A).

Temperature-dependent photoluminescence measurements between 20K and 300K were used to give internal quantum efficiency assessments: 30%, 25%, and 21%, for the G-, O-, and A-LEDs, respectively. The values are high compared with a typical value of 12% for c-plane MQWs emitting at 570nm. The decline in IQE for higher-indium-content quantum wells is attributed to a "larger internal polarization field which results in larger electron–hole wave function separation".

The behavior of the photoluminescence lifetime temperature dependence is also different from traditional c-plane MQWs. In particular, there is no red-blue-red shift ('S-curve') behavior. The researchers comment: "The absence of S-curve implies a significant reduction of localized potentials for MQWs grown on the nano-pyramid facets."

Under electrical injection (Figure 6), the turn-on voltage of the LEDs was around 3V. At higher currents the voltage increases significantly to 6V at 200mA, higher than usual for c-plane LEDs. The researchers

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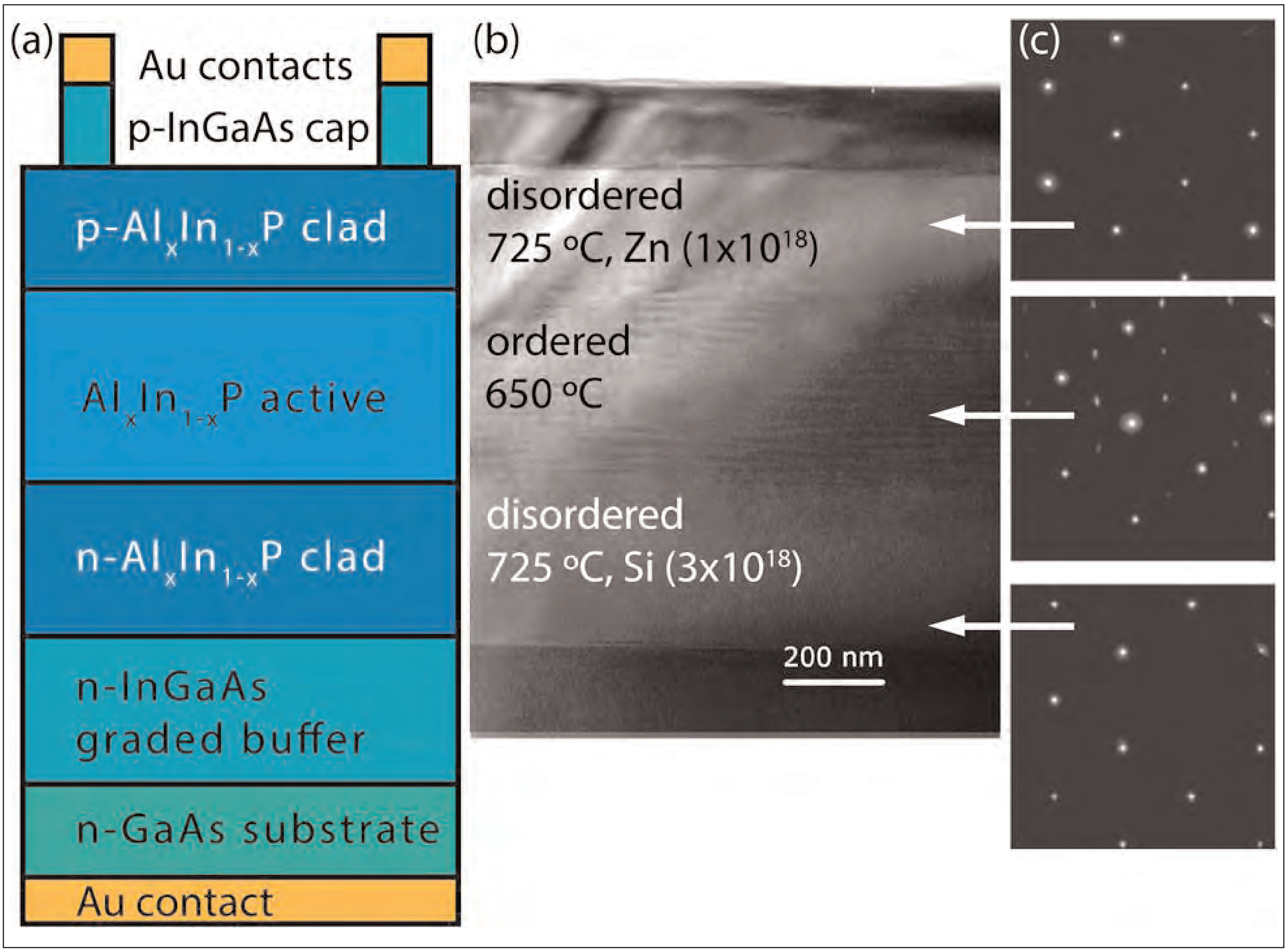

Figure 7. (a) Schematic of AlInP double-heterostructure LED device on graded InGaAs virtual substrate. (b) Transmission electron micrograph (TEM) of typical order-disorder heterostructure LED (device 1) with $Al_{0.39}In_{0.41}P$. (c) Transmission electron diffraction show both variants of CuPt-B type ordering occur in active layer, but ordering is suppressed in cladding.

believe that the diodes had high series resistance due to an imperfect contact between the ITO layer and the corrugated surface of the nanopyramid array.

Light output from the devices is slow to turn on, particularly in the longer wavelength A-LED, which does not operate before 40mA. This problem is attributed to current leakage effects. A high amount of defects in the base and apex regions is blamed.

With increased current the spectrum peak of light output undergoes a blueshift of 13nm, 25nm, and 50nm, for the G-, O-, and A-LEDs, respectively. "These blue-shift values are, nevertheless, still relatively small compared with that in a c-plane MQW," the researchers point out.

The indium composition gradient leads to rather broad emission spectra with full-width at half-maximum values, respectively, for the G-, O-, and A-LEDs of 60nm, 80nm, and 110nm. The researchers see possible applications for LEDs with even broader spectra as phosphor-free white-light LEDs.

Order–disorder route to amber–green

Researchers based in the USA have used a double-heterostructuring based on order–disorder properties of aluminium indium phosphide (AlInP) to produce 'amber–green' LEDs [Theresa M. Christian et al, J. Appl. Phys., vol114, p074505, 2013]. The research involved collaboration of National Renewable Energy Laboratory (NREL), University of Colorado Boulder, and Massachusetts Institute of Technology.

Copper-platinum B-type ordering in AlInP consists of spontaneous segregation into alternating aluminium- and indium-rich (111) planes. One effect of the ordering is expected to be a reduced bandgap. A similar order–disorder structure is used in high-brightness aluminium gallium indium phosphide (AlGa)InP LEDs.

The epitaxial structures were produced on gallium arsenide (GaAs) in a Thomas Swan/Aixtron low-pressure MOCVD system with a close-coupled showerhead. Growth began with a 250nm homoepitaxial layer of GaAs before applying compressively graded InGaAs

Table 2. Selected properties of the AlInP devices.

	Substrate	Al fraction	Active region	EL peak (300K)
Device 1	Miscut 6A	0.39	400nm	566 nm
Device 2	Miscut 6A	0.36	300nm	600 nm
Device 2B	(111)B	0.36	300nm	586 nm

buffer with lattice mismatch rate of 0.5%/μm. The 'virtual substrate' structure was capped with a constant composition 0.7μm InGaAs buffer layer.

The LED layers consisted of a double heterostructure of AlInP n- and p-type cladding around an undoped active region (Figure 7). The cladding layers were grown at 725ºC and the active region at 650ºC. The lower temperature growth of the active region was designed to promote ordering.

An InGaAs cap on the p-cladding was used for ohmic contact with gold electrodes. The epitaxial structure was annealed at 425ºC for a minute after growth. The gold on the p-side was in a grid form that was used as a mask for etch removal of the underlying InGaAs cap.

Three sample types were produced (Table 2) with different AlInP compositions. Also in one case a (111)B substrate was used to suppress atomic ordering of the AlInP alloy. The other devices were grown on (100) substrates miscut 6º in the $(\bar{1}\bar{1}1)$ direction ('Miscut 6A'). Material grown on such miscut substrates tends to demonstrate improved material qualities such as better compositional homogeneity and surface smoothness.

The researchers comment: "Based on the reported results for bulk epilayer $Al_xIn_{1-x}P$ films, we anticipate that bandgap differences between cladding and active layers in excess of 150meV can be achieved by optimizing our control of material ordering." However, the devices actually produced were estimated to have bandgap shifts of only 20–60meV, indicating room for improvement.

A reference device with GaInP active region and AlGaInP cladding was also produced on Miscut 6A substrates. The device used as reference was the brightest among several produced using conditions similar to those for the AlInP devices. Commercial $Ga_{0.51}In_{0.49}P$ LEDs can achieve external quantum efficiencies of more than 55%.

Pulsed current measurements were used to avoid self-heating affecting light output measurements. The light outputs of the 566nm (amber–green) and 600nm (orange ~ 590–635nm) emitting devices at $1A/cm^2$ injection current density were, respectively, 23% and 39% that of the ~650nm (red ~ 700–635nm) standard GaInP reference device (Figure 8).

The researchers comment: "The performance of the $Al_xIn_{1-x}P$ devices relative to a similar-quality, unoptimized $Ga_{0.5}1In_{0.49}P$ device strongly indicate that an $Al_xIn_{1-x}P$ material system holds promise for effective light emission in the amber–green wavelength range."

The disordered device 2B was compared with the ordered active region device 2. The researchers recognized the likely poorer quality of device 2B since it was grown using a process optimized for device 2. The light outputs were therefore normalized separately at $1A/cm^2$ to remove the material quality effect.

Beyond $1A/cm^2$, the light output from device 2 was relatively greater than for device 2B. At $40A/cm^2$, the boost from using an order–disorder heterostructure was a factor of three improvement in light output of device 2 over device 2B. ■

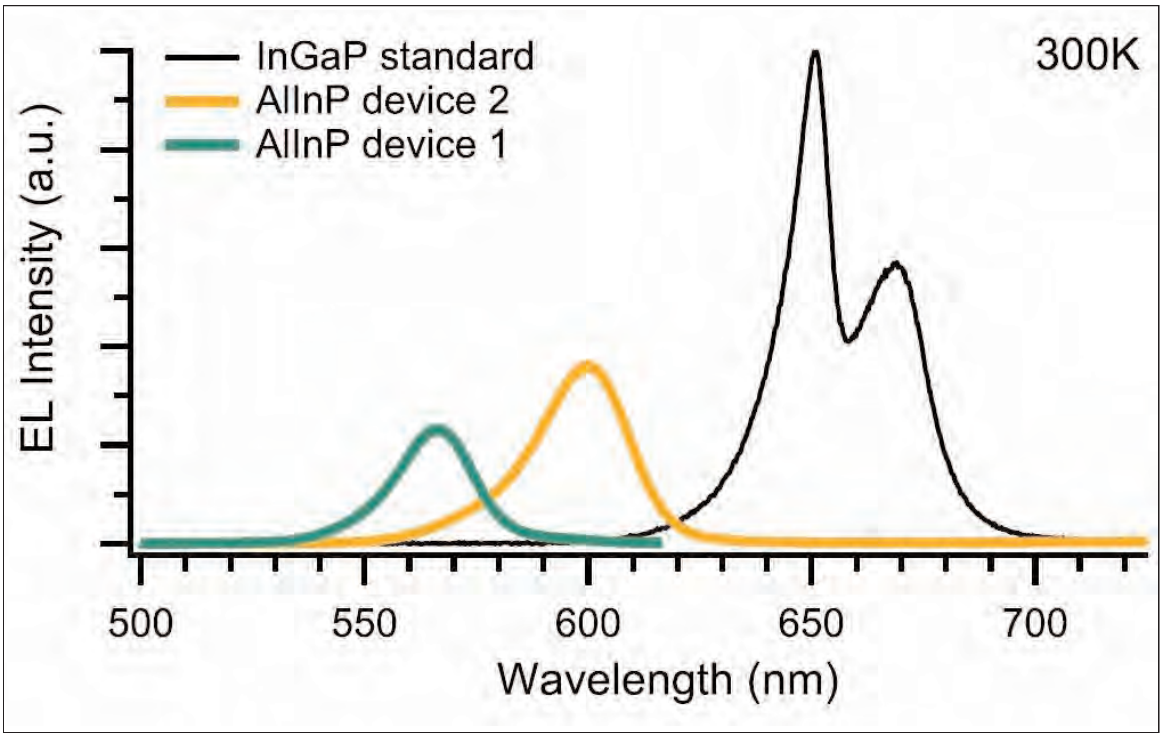

Figure 8. Comparison of room-temperature electroluminescence spectra for devices with mesa area $0.1cm^2$ at 100mA drive current (density $1A/cm^2$) for both $Al_xIn_{1-x}P$ LEDs compared with reference $Ga_{0.51}In_{0.49}P$ LED.