Metal nanoparticle plasmon push for III-nitride light-emitting diodes

Red- and white-emitting devices benefit from resonance between free-electron states and semiconductor active regions and phosphors, Mike Cooke reports.

Present-day reality is far from theoretical limits when it comes to the performance of light-emitting diodes (LEDs) based on indium gallium nitride (InGaN) compound semiconductors. Ways to edge towards the physical boundary come slowly and many concepts are brought into play.

Two recent works have used localized surface plasmons (LSPs) on metal nanoparticles (NPs) to step up red and white LED performance. Plasmons describe oscillations of free-electron density in metals. Confining plasmons in NPs create resonant LSPs, dependent on the particle composition and size.

Here, we look at this recent work.

Red boost

Japan's Osaka University has combined silver (Ag) nanoparticles with europium-doped gallium nitride (GaN:Eu) LEDs to boost red electroluminescence by a factor of two [Jun Tatebayashi et al Appl. Phys. Express, vol12, p095003, 2019]. The output power enhancement is attributed to coupling between localized surface plasmons on the Ag NPs and the electron transitions in the Eu ions that produce red photons.

The GaN:Eu LEDs operate through ~620nm-wavelength transitions in the electronic state of the Eu^{3+} ions, rather than the band-to-band transitions of InGaN devices, for which ~520nm green wavelengths are a struggle to obtain efficiently.

The research team points out that stable, narrow-wavelength GaN:Eu red LEDs "have recently reached output-powers respectable for commercialization." They suggest that further performance enhancements could lead to applications such as in micro-LED displays with red, green and blue emitters on a common GaN platform.

The GaN layers were applied using metal-organic vapor phase epitaxy (MOVPE) on sapphire via trimethyl-gallium and ammonia precursors (Figure 1). The GaN:Eu layer, co-doped with oxygen (O), used in addition bis(n-propyl-tetramethyl-cyclopenta-dienyl)europium ($EuCp^{pm}_2$) and argon-diluted O_2 sources. The n- and p-type silicon and magnesium doping was achieved by adding monomethylsilane and bis(cyclopentadienyl)-magnesium (Cp_2Mg), respectively.

The growth sequence was: 530ºC GaN buffer, 1.5μm 1200ºC undoped GaN, 2.4μm n-GaN contact, 100nm 960ºC GaN:Eu,O active layer, and 1050ºC p-GaN contact.

Further processing consisted of 10-minute 800ºC annealing in nitrogen to activate the p-GaN doping, formation of self-assembled Ag nanoparticles, 150nm indium tin oxide (ITO) sputtered p-contact, and chromium/gold (Cr/Au) metal contact electron-beam deposition.

Inductively coupled plasma etch was used to expose the n-GaN layer for the metal contact deposition. The final devices were 1mmx1mm in lateral dimensions.

The nanoparticle formation consisted of electron-beam deposition of a silver film, followed by annealing at 200ºC for 30 minutes in nitrogen.

Photoluminescence (PL) experiments on the epitaxial material with Ag nanoparticles showed a 622.4nm peak at room temperature. The peak shifted to 621.8nm at 10K. The emission was attributed to $^5D_0$–$^7F_2$ transitions in the Eu. At 10K, there are also

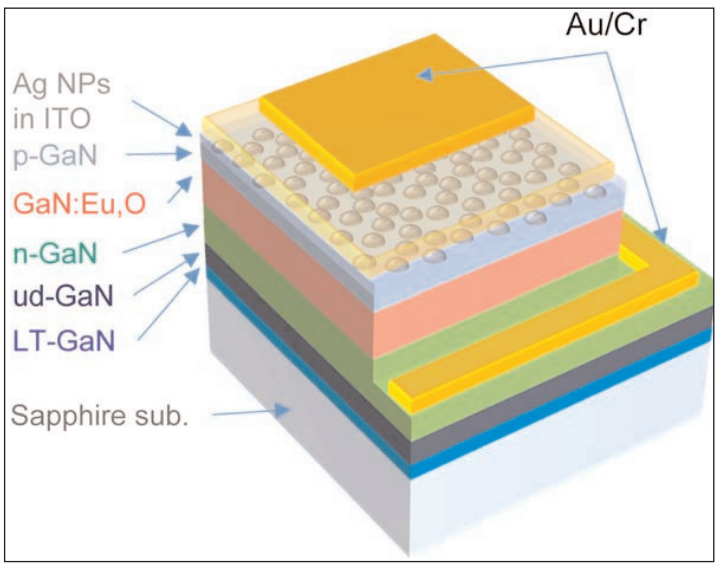

Figure 1. Schematic of fabricated LEDs.

"several" lesser peaks either side of the main one. [I see two (with a broad ~10nm hump on the short-wavelength side) in the image in the paper, but maybe these break up into "several" at higher resolution.] These peaks become less clearly defined at room temperature. The different peaks are attributed to variations in the electromagnetic environment of the Eu^{3+} ions in the GaN crystal structure.

"This is a result of the existence of defects such as Ga and N vacancies, as well as carbon, oxygen and hydrogen, yielding various 'Eu incorporation sites', and also modifies the transition probabilities of each Eu site," the team explains.

The intensity of the emissions generally increased with the thickness of the Ag film used to create the nanoparticles — at 20nm the intensity was 3.4x that for the bare material at room temperature (6.65x at 10K). There was a slight intensity dip initially with 5nm Ag, before enhancements set in with thicker Ag films.

The researchers comment: "The observed enhancement of the luminescence intensity is predominantly a result of coupling of the Eu^{3+} luminescence to the localized surface plasmon modes of Ag nanoparticles, although a small increase due to reflection at the GaN/Ag nanoparticles interface might be expected after the formation of Ag nanoparticles."

The PL studies did not show near-band-edge emissions from the GaN material (in the near ultraviolet) or 'yellow luminescence' associated with crystal defects. The team writes: "This indicates that electron-hole pairs generated in the GaN host can be efficiently captured to the trap level responsible for energy transfer from the host material to the Eu^{3+} ion."

Time-resolved PL analysis at 10K found that the decay time with 20nm Ag nanoparticles was shorter than that for bare material — 204μs, compared with 263μs. The 1.3 increased decay probability was taken as deriving from the coupling between the Eu ions and the localized surface plasmons of the Ag nanoparticles. In fact, the decay time was minimized at 194μs with nanoparticles created with 15nm Ag films. The researchers tentatively attribute the increase with 20nm Ag to "the irregular shape and large size variation" of the nanoparticles reducing the coupling with the Eu ions.

The LSP-ion coupling is seen as being rather small, compared with conventional InGaN quantum well and surface plasmon structures reported in the scientific literature. The researchers suggest that this is due to the much thicker GaN:Eu,O layer, compared with quantum wells — 100nm versus 1–3nm, typically. Resonance effects tend to drop off rapidly with distance.

Electroluminescence performance was assessed for radiation extracted out of the sapphire back-side of the device (Figure 2). The onset of light emission came at around 10mA current injection. The researchers say

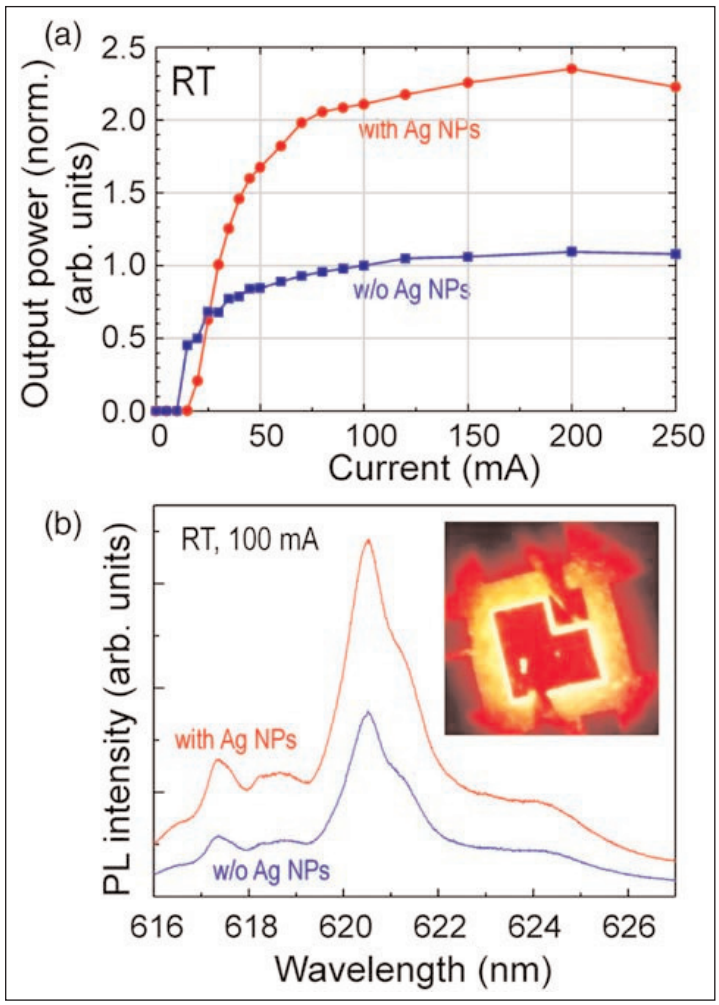

Figure 2. (a) Output-power versus injection current of fabricated GaN-Eu-based LEDs with and without Ag nanoparticles. (b) EL spectra of GaN:Eu-based LEDs under 100mA injection current. Inset: microscopic image of red LEDs.

that optimization of the thickness and doping density of the p-GaN layer is required to reduce current leakage while maintaining coupling efficiency between the localized surface plasmons and GaN:Eu layers. The light output saturated around 100mA. The device with Ag nanoparticles had 2.1x the output without the particles at 100mA.

While it is tempting to increase the emission by increasing the Eu concentration, this runs the risk of reducing crystal quality and thus the light emission performance.

White luminous efficiency and color rendering

Researchers based in China have combined phosphors, quantum dots, and metal nanoparticles to create blue-to-white light converters for InGaN LEDs with simultaneously improved luminous efficiency (LE) and color rendering [Rongqiao Wan et al, Optics Letters, vol44, p4155, 201]. Often improved color rendering comes at the cost of reduced LE.

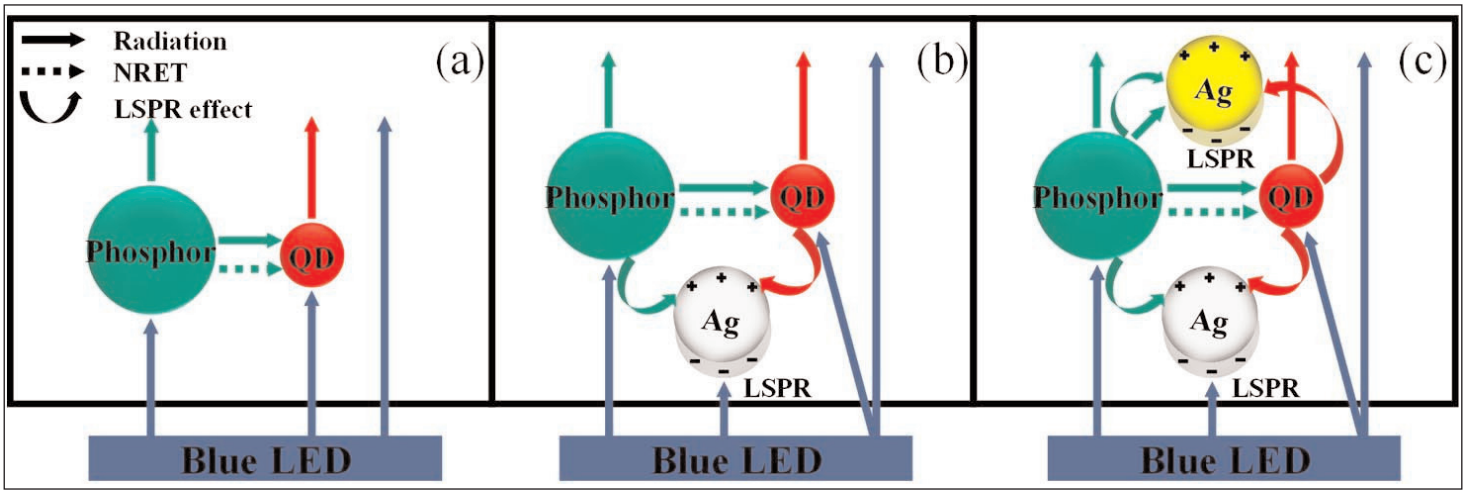

Figure 3. Schematic mechanisms and energy transfer paths for (a) wo-WLEDs; (b) Ag-WLEDs; (c) AgAu-WLEDs.

The approach adopted by Central South University, Semiconductor Lighting Technology Research and Development Center, and University of Chinese Academy of Sciences, enables a broader spectrum of light over the visible range, filling in the red end of the spectrum, compared with the low-cost white LEDs using yellow phosphors that are presently in mass production.

The researchers combined green- and red-emitting phosphors with silver (Ag) and gold (Au) nanoparticles. The broadband green emitter consisted of cerium-doped lutetium aluminium garnet (LuAG:Ce, $Al_5Lu_3O_{12}$). Core/shell cadmium selenide/zinc sulfide (CdSe/ZnS) quantum dots (QDs) in toluene solvent provided a narrowband blue-to-red converter. The Ag nanoparticles, on average, were 15nm diameter, and the Au nanoparticles 70nm diameter. The nanoparticles were dispersed in toluene.

The materials were mixed into silicone gel, and the mixture was placed in vacuum for 90 minutes to remove the toluene. The gel was then dropped onto 10milx23mil 451nm blue LED chips in a lead frame. The blue electroluminescence of the LEDs had a full-width at half maximum (FWHM) of 17nm. Thermal curing at 130ºC lasted 15 minutes. All the samples contained the green phosphor and red QDs, but some also contained silver (Ag-WLEDs) or silver and gold (AgAu-WLEDs) nanoparticles to give white LEDs. The samples without nanoparticles were designated wo-WLEDs.

Table 1. CRI, CCT and LE of Ag-WLEDs with varied nanoparticle concentrations.

Ag NPs (ppm)	Current density (A/cm^2)	CRI	CCT (K)	LE (lm/W)
0	4	89	5800	81
0	40	90.8	6000	61
1	4	90	5500	82
1	40	92	5700	61
3	4	93	5100	87
3	40	91	5200	66
5	4	93.6	5230	86
5	40	92.6	5450	64

Table 2. CRI, CCT and LE of AgAu-LED with varied Au nanoparticle concentrations and constant 3ppm Ag nanoparticles.

Ag NPs (ppm)	Current density (A/cm^2)	CRI	CCT (K)	LE (lm/W)
0	4	93	5100	87
0	40	91	5200	66
0.5	4	92	4750	89
0.5	40	89	4880	67
1	4	93.2	5070	92
1	40	92	5200	68
1.5	4	86	4950	92.5
1.5	40	84.3	5010	69.5

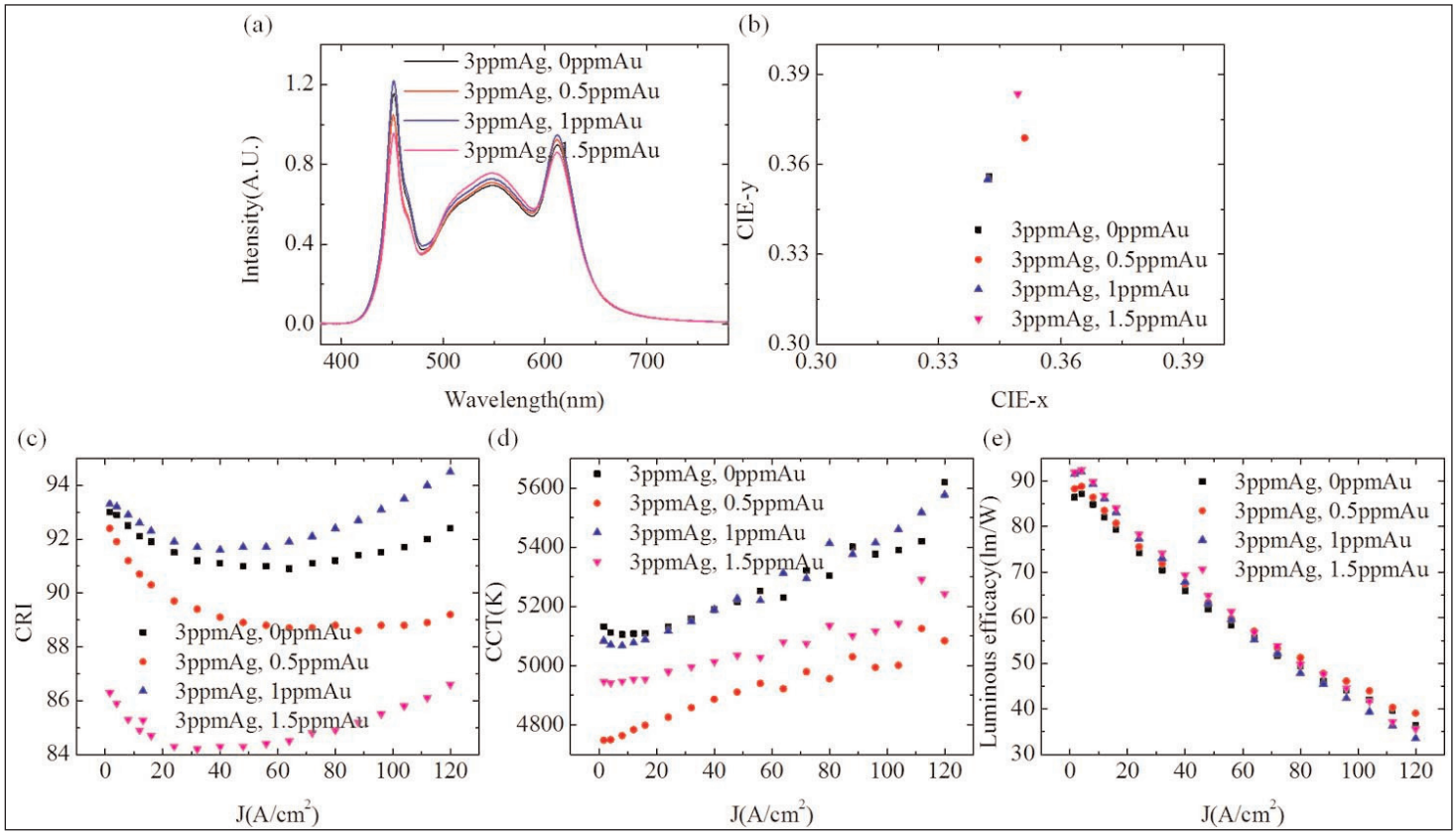

Figure 4. (a) Electroluminescence spectra of Ag-WLEDs and AgAu-WLEDs with varied concentration of Au nanoparticles and constant 3ppm Ag concentration under 20mA (16A/cm^2) injection current. (b) CIE-1931 chromaticity coordinates of AgAu-WLED, (c) CRI, (d) CCT, and (e) LE of Ag-WLEDs and AgAu-WLEDs versus current density.

The blue-to-white conversion layer was designed to take advantage of a variety of physical processes (Figure 3). The green (544nm wavelength under photoluminescence, 106nm FWHM) and red (613nm, 30nm FWHM) phosphors/QDs operated through Stokes processes of absorption of blue photons and emission of the longer-wavelength, lower-energy green and red light. Since green light has higher photon energy than red, some green-to-red conversion might also be expected. The use of QDs was also expected to add non-radiative energy transfer (NRET) channels between the green and red emitters.

The metal nanoparticles were also hoped to provide NRET enhancement. The Ag nanoparticles also absorbed the main blue light (454nm absorption peak) from the LED active region through localized surface plasmon resonance (LSPR). The team comments: "Due to the resonant light scattering effect, the absorption cross section of LuAG:Ce and CdSe/ZnS QDs for blue light increases, thus enhancing color conversion efficiency."

The Au nanoparticles were designed to have LSPR with the green emissions (531nm peak). The researchers also suggest that the resonance may provide an environment that gives Purcell-effect enhancement of spontaneous emission of the phosphor and QDs.

The researchers first investigated the improvements achievable with varied concentrations of Ag nanoparticles (Table 1). The peak color rendering index (CRI) of 93.6 was achieved with 5 parts per million (ppm) nanoparticles, by weight, and 4A/cm^2 current injection. Higher LE of 87 lumens per watt (lm/W) was found with 3ppm nanoparticles at 4A/cm^2. The 3ppm Ag-WLEDs also demonstrated the lowest correlated color temperature (CCT) of 5100K at 4A/cm^2. A low CCT indicates higher red and green content in the 'white' light, which is associated with 'warmer' illumination compared with regular white light.

The Ag-WLEDs were further enhanced with Au nanoparticles (Table 2). The Ag nanoparticles concentration was fixed at 3ppm. The incorporation of 1ppm Au nanoparticles enabled an increase in LE to 92lm/W at 4A/cm^2, while the CRI and CCT were 93.2 and 5070K, respectively. Increasing the injection current to 120A/cm^2 enhanced the CRI to 94.5 (Figure 4). With 1.5ppm Au nanoparticles the LE increased to 92.5lm/W at 4A/cm^2, but at the cost of reduced 86 CRI.

The team expects further enhancements from "package and energy transfer structure optimization" to reduce energy losses. ■

The author Mike Cooke has worked as a semiconductor and advanced technology journalist since 1997.