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Improved LEDs and photovoltaics by hybridization and nanostructuring

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Novel combinations of zinc oxide and gallium nitride offer enhanced efficiency, lifetime, and spectral coverage for next-generation optoelectronic devices.

Since the development of p-type doping of gallium nitride (GaN) in the early 1990s,[1–4] there has been rapid industrial development for optoelectronic devices based on alloys of GaN with aluminum and indium (AlInGaN), which span a direct bandgap from deep UV to IR, and are currently widely used in commercial white, UV, blue, and green LEDs.[5] This alloy system is now projected to provide a platform for the development of novel multi-junction photovoltaics (PVs) with an unprecedented fit to the solar spectrum.[6]

However, improving the efficiency of InGaN-based p-n junctions is a very complex and multifaceted task for a number of reasons. One concern is the losses due to strain fields linked to the polar nature of GaN.[7] A second problem is that the high refractive index of GaN (∼2.5) and the intrinsically planar surface of LED/PV structures creates light extraction and reflection issues (<15% of light escapes from a planar GaN/air interface as a result of total internal reflection, and a planar PV surface reflects >10% of incident light).

Third, there is a lack of native substrates. Cheap, large-area, epitaxially matched substrates are not commercially available, so alternative, but relatively expensive, small, insulating sapphire substrates are used. The electrical insulation imposes lateral device geometries (fewer devices per wafer) and causes power and efficiency limitations. The thermal insulation is a problem because LEDs/PVs dissipate most of their heat through conduction, and overheating severely impacts the output power, efficiency, and lifetime.[8] Fourth, asymmetric doping (p-GaN carrier concentration and mobility are lower than that of n-GaN) leads to efficiency issues at elevated junction currents.[9] And fifth, the integrity of the InGaN active layers is compromised for higher indium content.[10]

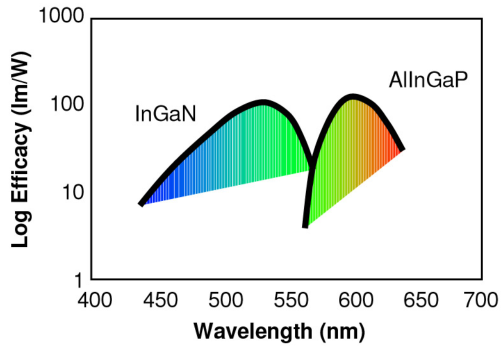

Figure 1. *Efficacy versus wavelength for state-of-the-art LEDs, showing exponential efficacy fall-off in the green.[14] InGaN: Indium gallium nitride. AlInGaP: Aluminum indium gallium phosphide.*

The fifth point is critical. It is the result of an n-GaN layer that must be grown on top of the InGaN active layer at a significantly higher growth temperature, Tg, than the InGaN in order to simultaneously obtain high structural quality and reasonable p-type doping. Tg is ∼1000°C for the GaN overlayer in conventional metal organic chemical vapor deposition (MOCVD). This temperature difference produces significant indium diffusion at the higher indium content required in the green portion of the spectrum and contributes to a 'green gap' in efficiency and reduced lifetime[11] (see Figure 1[12,13]). This problem is critical for LEDs in that it prevents the use of a red/green/blue approach for white lighting. The problem is also critical for PVs in that it prevents the capture of the solar spectrum near the sweet spot for efficiency.

Zinc oxide (ZnO) is a remarkable, multifunctional, and biocompatible direct-, wide-bandgap semiconductor, with a distinc-

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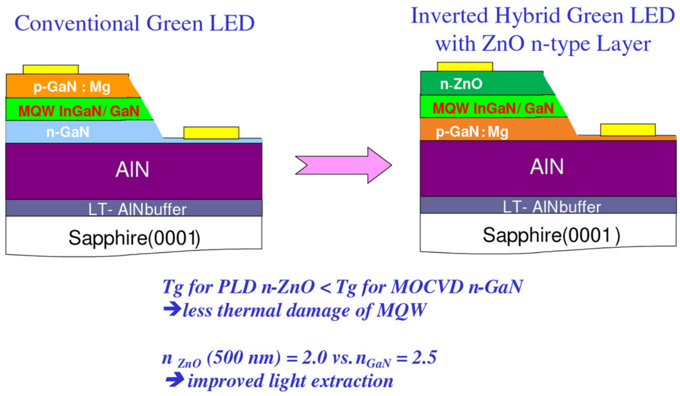

Figure 2. *Schematic showing an inverted LED structure with lower growth temperature (Tg) n-type zinc oxide (n-ZnO) (grown by pulsed laser deposition) substituted for n-type gallium nitride (n-GaN). MQW: Multi-quantum well. Mg: Magnesium. MOCVD: Metal organic chemical vapor deposition. p-GaN: p-Type GaN. AlN: Aluminum nitride. LT-AlNbuffer: Low-temperature AlN buffer.*

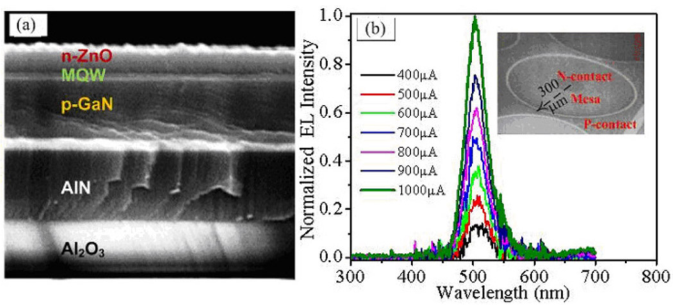

Figure 3. *(a) Cross-sectional scanning electron microscope (SEM) image of hybrid green LED showing the preserved integrity of the InGaN MQWs. (b) SEM image of device and the electroluminescence (EL) intensity spectrum for the green hybrid LED. Al_2O_3: Sapphire.*

tive property set and a unique potential for nanostructuring. Recently, there has been a surge of activity surrounding ZnO to the point where the number of publications now rivals that for GaN. Due to their similar crystal structures and bandgaps, ZnO and GaN can be combined in new ways, which opens up the prospect of novel optoelectronic devices. In preliminary studies,[2] we exploited this synergy in order to combat the diffusion of indium through a novel device architecture in which we substituted a lower Tg n-type ZnO layer for n-type GaN in an inverted n-ZnO/p-GaN heterojunction (see Figure 2). This design prevents indium from leaking and thus preserves the integrity of the InGaN underlayer (see Figure 3), which allows superior efficiency, lifetime, and spectral coverage. Such hybridization was found[15,16] to give an external quantum efficiency >35% (i.e., the percentage of injected current converted to emitted light), which is comparable to that of blue LEDs (see Figure 1).

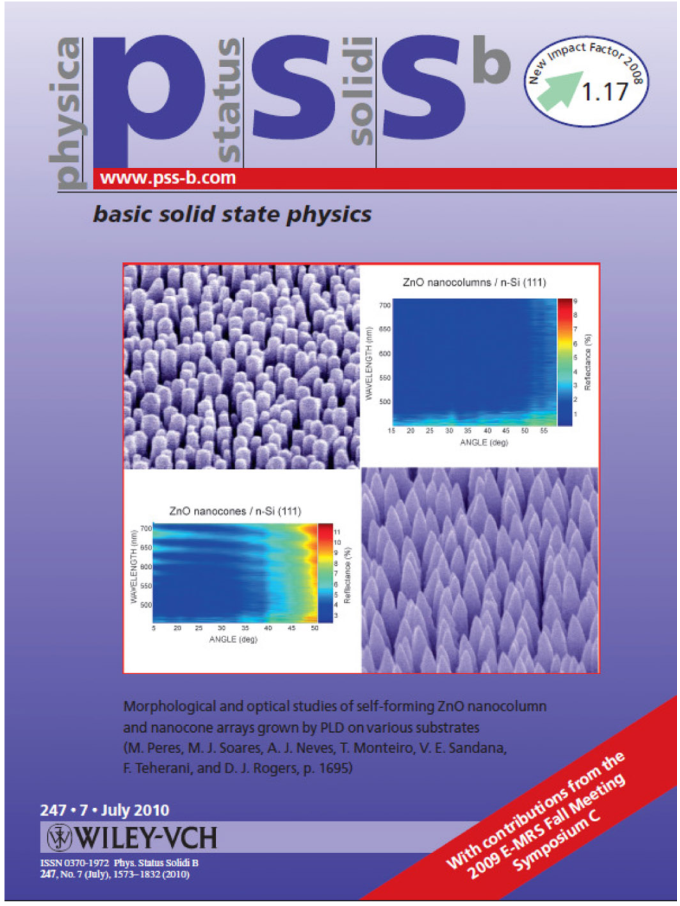

Figure 4. *Cover of Physica Status Solidi B showing SEM images of moth-eye-like ZnO nanostructure arrays and the anti-reflection (AR) performance as a function of angle and wavelength.*

More recently, we showed that pulsed laser deposition-grown ZnO top layers can play/combine roles other than just n-type conduction. This occurs by offering transparent conducting oxide (TCO) functionality. Currently, indium tin oxide (ITO) represents more than 80% of TCOs used in LEDs and PVs,[17] but ZnO is transparent to visible/near-UV wavelengths and can be equally as conductive as ITO when doped with aluminum. Thus, an (Al)ZnO (AZO) layer can double as an indium-free layer for current spreading.[18,19] Moreover, the replacement of ITO with AZO as a current-spreading layer is desirable from a technical, environmental, and economic perspective in that AZO is easier to fabricate than ITO, and because indium is toxic, relatively expensive, and in short supply.[20]

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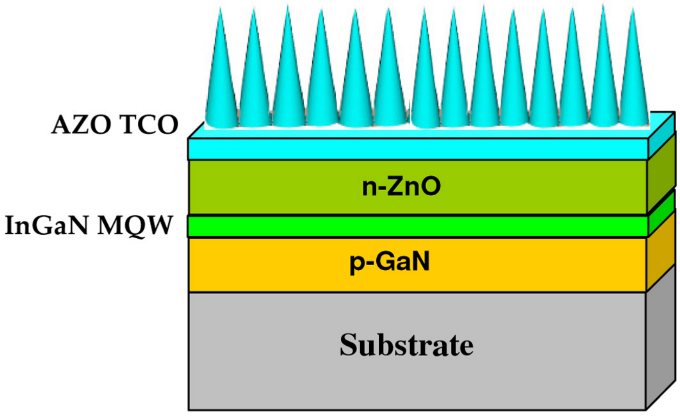

Figure 5. *Illustration of inverted n-ZnO/p-GaN junction with n-ZnO (AR) and AZO (TCO) coatings. AZO: Aluminum-doped ZnO. TCO: Transparent conductive oxide.*

The PLD ZnO layer also boosts device performance by enhancing light extraction in LEDs and eliminating reflection in PVs. First of all, ZnO has a lower refractive index (∼2 vs. n ∼ 2.5 for GaN), allowing more light to be coupled out of LEDs or into PVs. Second, we have developed know-how for surface nanostructuring, which enhances optical absorption for PVs and light extraction for LEDs, and thus further boosts overall efficiency. In PVs, conventional anti-reflection coatings (typically thin-film bilayers or surface roughening) usually only reduce the reflectance down to about 5–10%. To go beyond this, special surface treatments are needed.

The moth-eye-like nanoarrays[21] that we developed offer a much higher performance alternative, with <0.5% of reflected light for all visible wavelengths over incidence angles up to 60° from the normal (see Figure 4).[22] Moreover, the catalyst-free, self-forming nanostructuring can be realized as a modification of the AZO surface at minimal additional manufacturing cost (simply by changing the TCO growth conditions). In future, we envision combining such nanostructuring with the hybridization concepts in order to further boost the power, efficiency, lifetime, and cost-effectiveness for InGaN-based PVs and LEDs [23–25] (see Figure 5).

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