

# ZnO Thin Films & Nanostructures for Emerging Optoelectronic Applications

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## ABSTRACT

ZnO-based thin films and nanostructures are proposed for various emerging optoelectronic applications. AlZnO thin films are currently displacing ITO for many TCO applications due to recent improvements in attainable AZO conductivity combined with processing, cost and toxicity advantages. Advances in the channel mobilities and  $I_{on/off}$  ratios in ZnO-based TFTs have opened up the potential for use as a replacement for a-Si in AM-OLED and AM-LCD screens. Angular-dependent specular reflection measurements of self-forming, moth-eye-like, nanostructure arrays grown by PLD were seen to have <0.5% reflectivity over the whole visible spectrum for angles of incidence between 10 and 60 degrees. Such nanostructures may be useful for applications such as AR coatings on solar cells. Compliant ZnO layers on mismatched/amorphous substrates were shown to have potential for MOVPE regrowth of GaN. This approach could be used as a means to facilitate lift-off of GaN-based LEDs from insulating sapphire substrates and could allow the growth of InGaN-based solar cells on cheap substrates. The green gap in InGaN-based LEDs was combated by substituting low  $T_s$  PLD n-ZnO for MOCVD n-GaN in inverted hybrid heterojunctions. This approach maintained the integrity of the InGaN MQWs and gave LEDs with green emission at just over 510 nm. Hybrid n-ZnO/p-GaN heterojunctions were also seen to have the potential for UV (375 nm) EL, characteristic of ZnO NBE emission. This suggests that there was significant hole injection into the ZnO and that such LEDs could profit from the relatively high exciton binding energy of ZnO.

**Keywords:** ZnO, PLD, TCO, TFT, LED, Solar Cell, Nanostructure, InGaN

## 1. INTRODUCTION

ZnO is a remarkable multifunctional material with a direct wide bandgap, intrinsically high transparency over the whole visible range and a resistivity that can be tuned from semi-insulating right through to semi-metallic by doping. Table 1 compares some key properties of ZnO and GaN (the next most industrially-important semiconductor after Si).

Materials	Crystal Structure	Lattice constants		Band gap at RT (eV)	Cohesive energy (eV)	Melting point (K)	Exciton binding energy (meV)
		a (Å)	c (Å)				
ZnO	Wurtzite	3.249	5.207	3.37	1.89	2248	60
GaN	Wurtzite	3.189	5.185	3.39	2.24	1973	21

Table 1 Comparison of selected properties of ZnO and GaN (adapted from [1]).

The table reveals that ZnO and GaN are very similar materials, with the same wurtzite crystal structure, comparable lattice-constants/bandgaps and high cohesive-energies/melting points. Like GaN, ZnO is also a strongly polar material and it exhibits one of the highest piezoelectric responses of all semiconductors. There are some significant differences between ZnO and GaN, however. In particular, wet etching is possible for ZnO, with nearly all dilute acids and alkalis, whereas GaN requires HF or plasma etching. ZnO also shows a

higher radiation resistance and is abundant (unlike Ga), so ZnO cost is low. Finally, ZnO is biocompatible. Indeed, it is one of the ingredients of vitamin pills. The distinctive property set has led to a number of industrial applications for ZnO-based electronics. A recent market study [2] identified the 4 main current uses as conductive & optical coatings, gas sensors, Surface Acoustic Wave (SAW) devices and varistors, amounting to an combined annual market of about half a billion dollars in 2009. Recently, there has been a surge of research activity focused on ZnO. Figure 1 shows the evolution over time of the number of publications per year in Applied Physics Letters for three direct wide bandgap materials: ZnO, GaN and SiC.

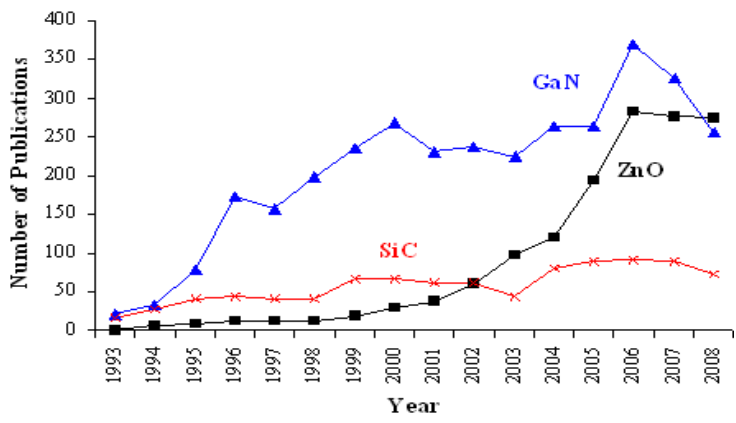


Figure 1. Number of publications/year in Applied Physics Letters for ZnO, GaN & SiC.

The graph reveals that the number of publications for ZnO has shown exponential growth since the mid 1990s and is now comparable with that for GaN. The number of publications for SiC, on the other hand, is much lower and has not progressed significantly over the same period. There are numerous breakthroughs driving this, including the know-how for band gap engineering, studies of self forming laser cavities, availability of high quality ZnO substrates, suggestion that doped ZnO could be a Room Temperature (RT) ferromagnetic semiconductor, stimulated excitonic emission at temperatures over 550K, demonstration of schottky & ohmic contact know-how, high quality epitaxy, the development of novel ZnO-based Amorphous Oxide Semiconductors (AOS) with industrially relevant conductivities ( $\sigma$ ) and mobilities ( $\mu$ ), reports of p-type doping, homojunction Light-Emitting Diodes (LEDs) & Laser Diodes (LDs), RT ultraviolet (UV) photonic crystal lasing, Transparent Thin Film Transistors (TTFT), a 2 dimensional electron gas & the fractional quantum Hall effect. A comprehensive overview of these developments is given by Ozgur et al. [3]. ZnO has also shown itself to be a very important nanomaterial. Figure 2 shows the evolution over time of the number of publications/year in Nanoletters for ZnO, GaN and carbon nanotubes (CNT).

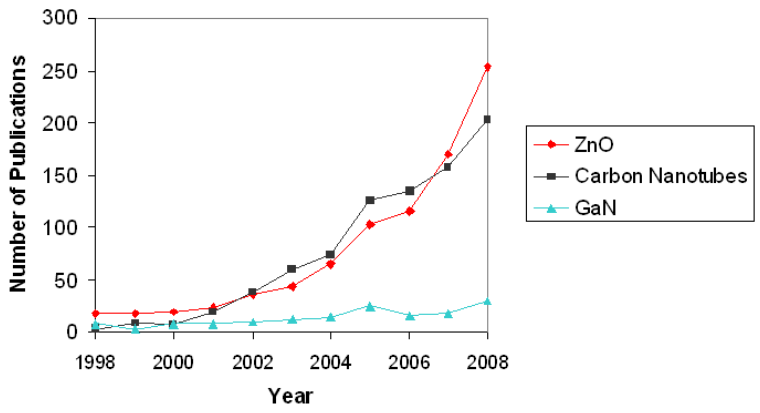


Figure 2. The evolution of the number of publications/year in Nanoletters for ZnO, GaN & CNT.

This graph shows that while there are far fewer publications on nanostructured GaN, there has been an exponential growth in publications on nanostructured ZnO, such that their number now exceeds that for CNT. Indeed, a survey, by Thomson-Reuters, published in Physics World in 2009 recorded more publications dedicated to nano ZnO than dedicated to the whole of thin film semiconductors. There are many reasons for this, including the ease of fabricating ZnO nanostructures by various techniques and the large family of nanostructures that can be obtained. This remarkable propensity for miniaturization has led to claims that nanostructures of ZnO might even have a key role to play in beyond-lithography electronics [4]. Figure 4 shows a forecast of the ZnO-based electronics market, which came out in 2009 [2].

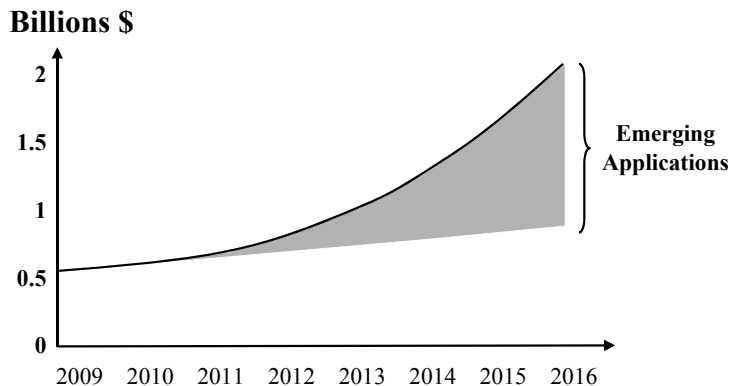
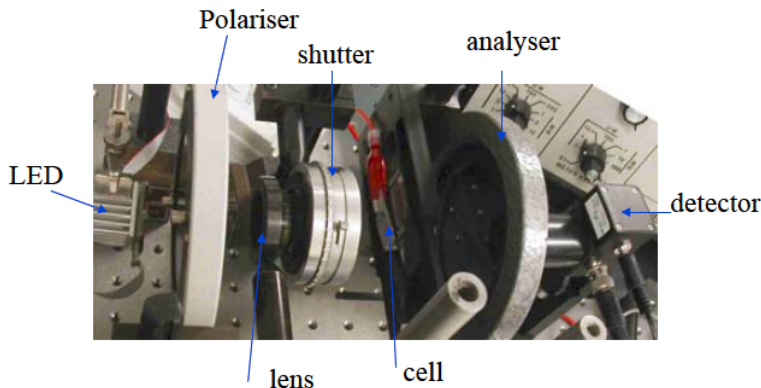


Figure 4. A forecast of the ZnO based electronics market.

The whole ZnO-based electronics market was estimated to be worth about 0.5 billion dollars in 2009 and predicted to grow to over 2 billion dollars by 2016. By 2016, 65% of the market is predicted to be made up of emerging applications. Four key emerging applications were identified in the study: photovoltaics, displays, LEDs and sensors (Gas, UV & Bio). In this paper, we illustrate how ZnO-based thin films and nanostructures grown by Pulsed Laser Deposition (PLD) can respond to current issues in some of these applications.

## 2. EXPERIMENT

ZnO thin films and nanostructures were grown on various substrates by PLD, as described elsewhere [5, 6]. Scanning Electron Microscopy (SEM) was conducted using a Hitachi S4800 field emission system. TTFT electrical characteristics were studied using a dual-source dc power supply, a Fluke multimeter and a Keithley 2400 source-meter. Liquid crystal characteristics were tested using the following set-up:



### 3. RESULTS & DISCUSSION

#### 3.1 ZnO as a Transparent Conductive Oxide

Up till present, the most widely used Transparent Conducting Oxide (TCO) has been Sn-doped  $\text{In}_2\text{O}_3$  (ITO). Recently, there has been a trend towards the substitution of wurtzite ZnO for ITO (particularly Al doped ZnO (AZO)). There are several reasons for this. Firstly, In is toxic, rare and costly, none of which apply to ZnO. Secondly, ZnO can be readily fabricated in crystalline form at relatively low temperatures compared with ITO [7]. Thirdly, ZnO is easier to process due to a greater amenability to chemical etching and a superior resistance to hydrogen plasmas than ITO. Fourthly, the properties of ZnO can be readily tuned by doping. For instance, doping with F gives ZnO the highest optical transparency and the lowest plasma frequency of all TCOs. Finally, both the  $\mu$  and  $\sigma$  attainable with ZnO have improved considerably over recent years and AZO can now give resistivities comparable with ITO [8]. These properties have led to the adoption of ZnO for a number of TCO applications, such as transparent coatings for filtering of UV light and transparent contacts for use in flat panel displays, solar cells and LEDs. Figure 5 shows a schematic and the response of a liquid crystal with ZnO-based transparent contacts grown on glass substrates by PLD.

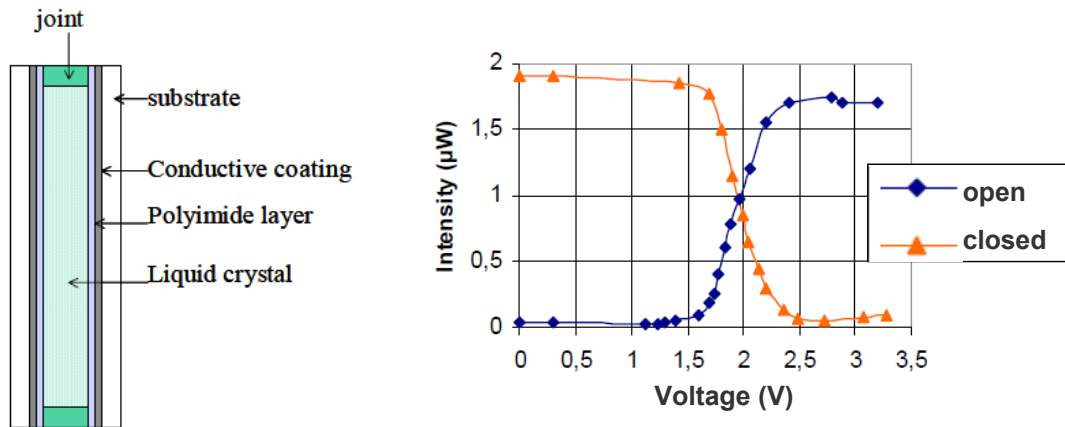


Figure 5. Schematic and open/closed transmissivity for a liquid crystal pixel activated via a ZnO TCO layer.

#### 3.2 ZnO-Based Transparent Thin Film Transistors

Recently, there has been a surge of activity in the development of TFT based on ZnO for use in applications such as Active Matrix Liquid Crystal Displays (AMLCD), electronic paper and flexible organic LED (OLED) panels. Although ZnO based TFTs are not a new concept [9], the new generation exhibits high on-off ratios ( $>10^6$ ) and a higher channel  $\mu$  than the Si-based devices, which are currently used as select transistor drivers in AMLCD and systems-on-glass. Two main ZnO TFT variants, employing either wurtzite [10] or amorphous ZnO alloys [11] as channels, have emerged. Figure 6 shows a schematic plus transfer and output characteristics for a staggered back-gate TFT with a wurtzite ZnO channel grown by PLD [12].

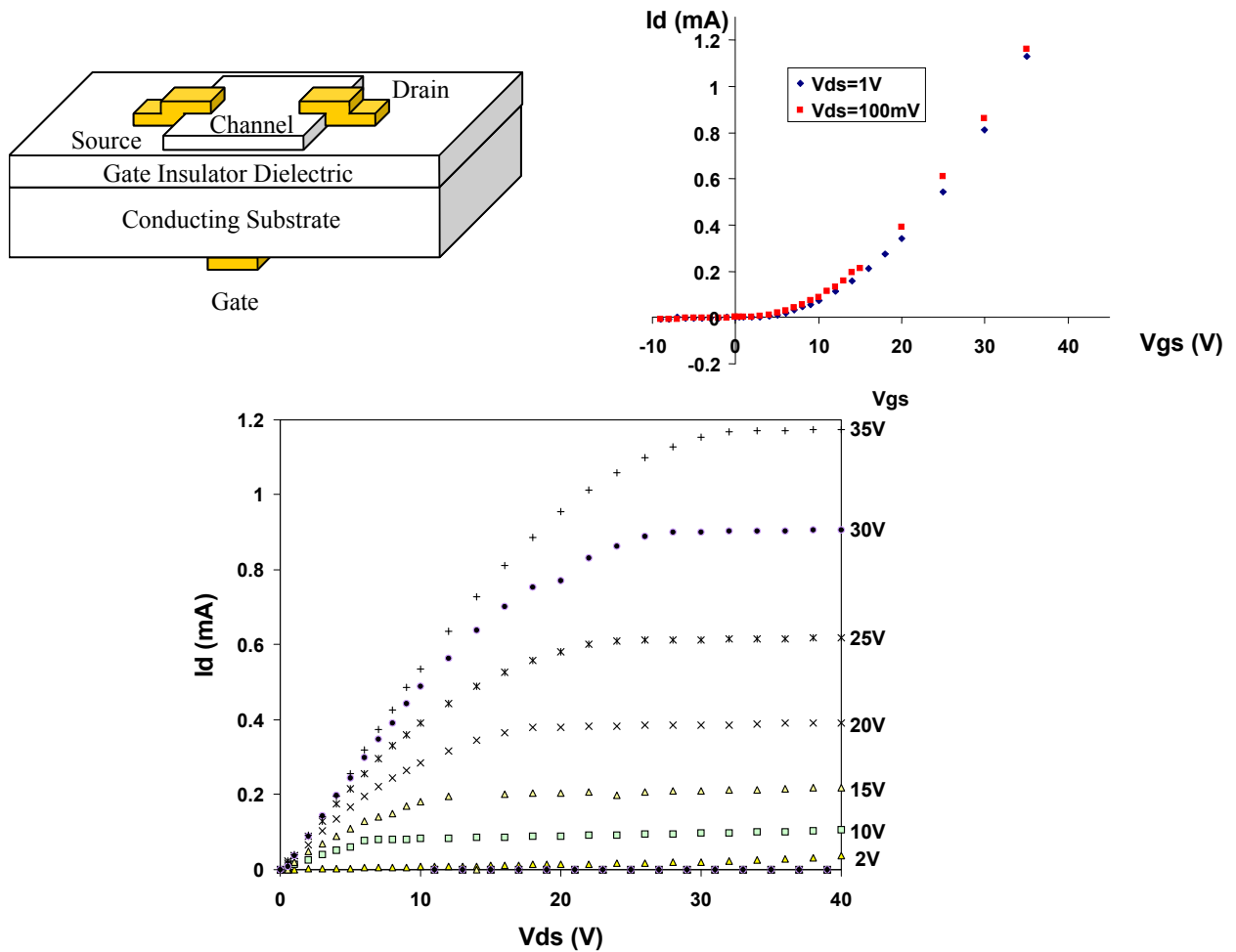


Figure 6. Schematic, transfer characteristic and output characteristics of a staggered back-gate TTFT [12].

The transfer characteristic (top) is rectifying, confirming transistor behaviour in the device. The  $V_{ON}$  is about 0V, which suggests that neither the electron nor the trap densities in the channel were too high. This device exhibited enhancement-mode behaviour, which is good for both energy efficiency (off-state is the power-down condition) and simplified circuit design. The lower (output) characteristics all showed “pinch-off” and “hard-saturation” (a plateauing of  $I_d$  above a certain  $V_{ds}$ ), which suggests that the whole channel could be depleted of electrons. The  $I_d$  is in the mA range, which is relatively large/good for a ZnO-based TFT. Such TFTs offer several advantages over incumbent Si-based devices. First of all, they are transparent, so that generally more light can be transmitted through each pixel, yielding a brighter, more efficient, display. This also means that the aperture ratio can be increased, so as to give smaller pixels. Next, state-of-the-art wurtzite ZnO and amorphous InGaZnO (a-IGZO) TTFTs now exhibit channel  $\mu$  as good as  $250\text{cm}^2/\text{Vs}$  and  $12\text{cm}^2/\text{Vs}$ , respectively, as compared with typical values of  $100\text{cm}^2/\text{Vs}$  and  $1\text{cm}^2/\text{Vs}$  for poly-Si and a-Si [13]. This gives faster device operation, which leads to a quicker response and an increased refresh rate. In addition, because of their wide bandgap, the ZnO based TTFTs have reduced sensitivity to light (ambient light has no significant effect on the current–voltage characteristics) and less degradation on exposure to light compared with their a-Si counterparts. TTFTs made with a-IGZO are of particular significance because they give excellent performance when fabricated at RT, can be fabricated in large area format, are lighter and have better uniformity of properties (due, in part, to a lack of grain-boundaries). Moreover, their performance is stable and reproducible during and after repetitive bending, so they are compatibility with flexible substrates.

This resolves the existing trade-off between processing temperature and device performance and allows fabrication on inexpensive heat-sensitive substrates such as transparent polymers or paper (poly-Si deposition temperature is too high for many flexible polymer substrates).

### 3.3 Use of ZnO in Photovoltaics

#### 3.3.1 ZnO as an Adaptation Layer to Grow Novel InGaN-based Solar Cells on Cheap Substrates

Most commercial solar cells are based on amorphous Si (a-Si) and polycrystalline Si (poly-Si) and show relatively poor efficiencies (5-7 % and 13-15%, respectively). Recently, there has been a lot of work to try to develop solar cells with higher efficiencies. Multijunction cells employing alloys of InGaN currently present the highest theoretical efficiency. This is because of InGaN bandgap engineering know-how giving them superior capacity to absorb the solar spectrum. Indeed, efficiencies over 60% have already been demonstrated [14] and values over 70% are possible, theoretically. A key problem, however, is that InGaN does not crystallize readily on cheap substrates, so the cost of such cells is prohibitively high. PLD ZnO has proven to be much more crystallographically compliant to non-native substrates than MOCVD GaN. With a view to exploiting this, ZnO layers were used as buffer layers for MOVPE regrowth of InGaN. Figure 7 shows an SEM image of a fracture cross-section of an InGaN/GaN/ZnO/Si (111) sample with ~ 21.5% In [15].

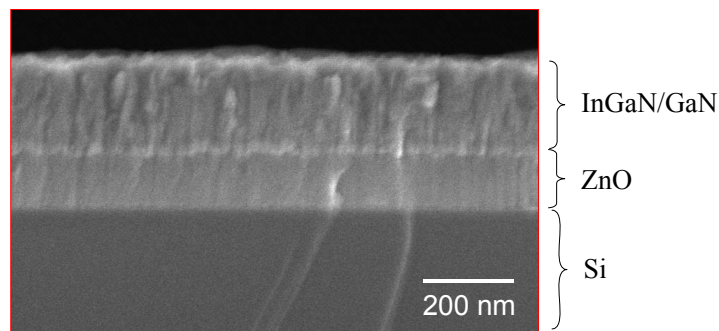


Figure 7. An SEM image of a fracture cross-section of an InGaN/GaN/ZnO/Si (111) sample.

The image reveals distinct InGaN/GaN and ZnO layers with a well-defined interface between the ZnO and InGaN/GaN. TEM [15] showed continuous lattice fringes across the interfaces with similar alignment and spacing in the InGaN/GaN and ZnO layers, suggesting that there had been epitaxial growth. Thus it was demonstrated that use of a PLD-grown ZnO buffer layer allows highly c-axis oriented wurtzite InGaN/GaN to be grown on Si substrates without removal of the amorphous SiO<sub>2</sub> layer. Such an approach may open the way to the integration of InGaN based photovoltaics (and other devices) on cheap amorphous substrates, such as glass.

#### 3.3.2 Nano ZnO as an Anti-Reflective (AR) Coating

Figure 8 shows SEM images of various self-forming ZnO nanostructures grown by PLD.

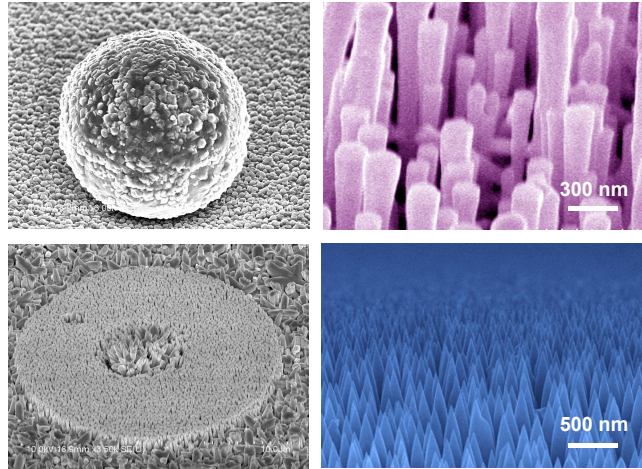


Figure 8 Examples of various self-forming ZnO nanostructures grown using PLD [16].

Figure 8 shows a microsphere assembly of nanocrystals, an annular microstructure made up of nanorods of different sizes, plus vertically aligned arrays of nanorods which either taper or broaden during growth. RT angular-dependent specular reflection measurements were conducted on the tapering “moth-eye type” version of these self-forming arrays, as shown in Figure 9 [17].

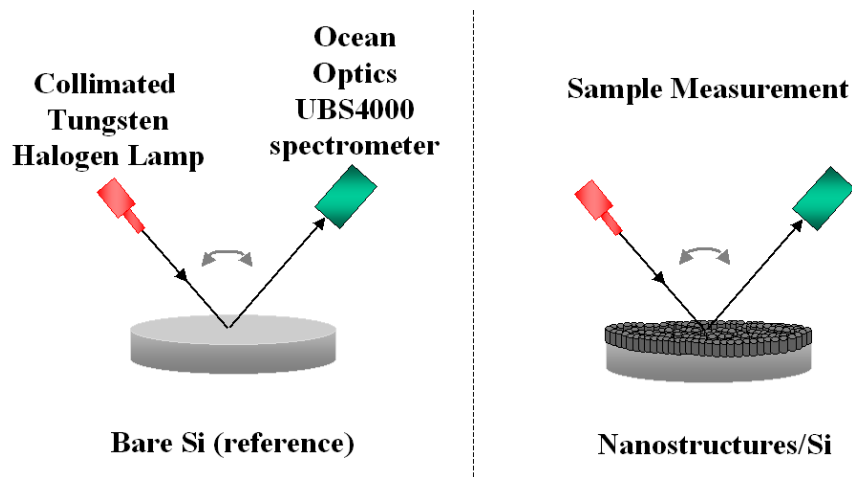


Figure 9. Schematics showing the angular-dependent specular reflection measurements set-up for a Si wafer with and without ZnO nanostructures on the surface.

These studies showed under 0.5% of reflected light between 450 nm to 800 nm for angles of incidence between 10 and 60 degrees. This indicates that such moth-eye type nanostructures could act as effective broad-band antireflection coatings for solar cells.



### 3.4 LEDs

#### 3.4.1 ZnO Sacrificial Substrate Solution for GaN based LEDs

The future development of GaN based LEDs and LDs is being hampered by constraints imposed by non-native *c*-sapphire (*c*-Al<sub>2</sub>O<sub>3</sub>) and 6H-SiC substrates. ZnO substrates have a lower lattice mismatch than either of these substrates but have not been adopted industrially because they tend to dissociate in the conventional GaN LED manufacturing process. Recently, the authors reported on a novel lower temperature approach to grow GaN on ZnO using MOVPE [18]. Figure 10 shows SEM image of MOVPE GaN grown on ZnO/*c*-Al<sub>2</sub>O<sub>3</sub>.

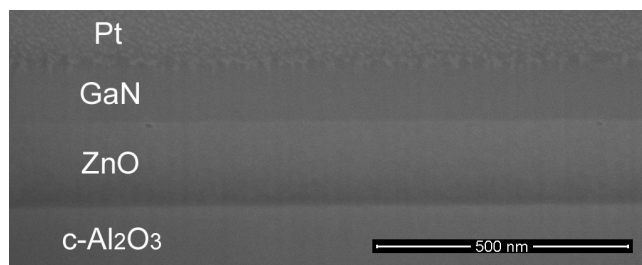


Figure 10. An SEM image of a fracture cross-section of MOVPE GaN grown on ZnO/*c*-Al<sub>2</sub>O<sub>3</sub>.

The image shows continuous GaN and ZnO with a smooth, well-defined interface. Since ZnO can be readily dissolved, subsequent lift-off of the GaN from insulating *c*-Al<sub>2</sub>O<sub>3</sub> substrates was demonstrated through preferential chemical etching of ZnO. Such an approach opens up the possibility of wafer-bonding GaN LEDs onto electrically/thermally conducting substrates, as illustrated in Figure 11.

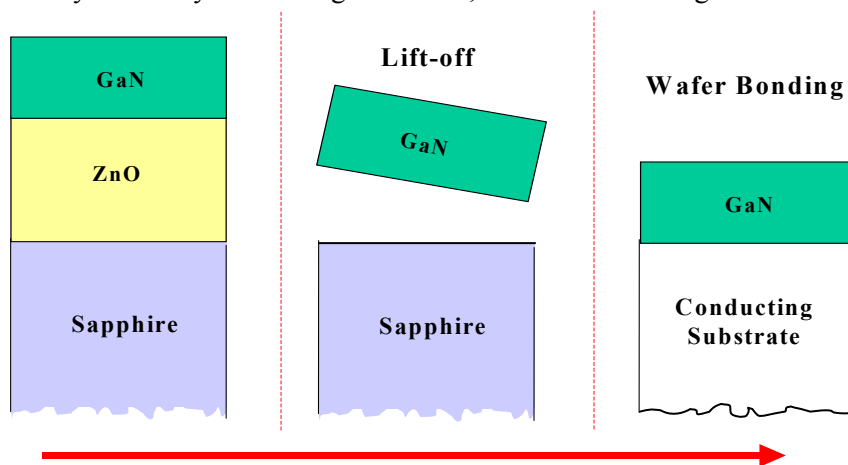


Figure 11. Schematic of GaN chemical lift-off via preferential chemical etching of ZnO followed by wafer bonding onto a conductive substrate.

Such an approach would allow vertical LED geometries with smaller footprints, improved heat dissipation, and reduced current crowding. These would, in turn, boost wafer yield and device performance in terms of efficiency, lifetime and brightness.



### 3.4.2 Hybrid UV LEDs

ZnO has been proposed as an active material for use in LEDs. One of the main driving forces for this is the superior stability of the ZnO free exciton (table 1 shows that ZnO has an exciton binding energy of 60 meV, vs. 21meV for GaN) [19]. A key roadblock, however, is the development of reliable p-type doping. Indeed, high levels of p-type doping, are hard to achieve in ZnO. This is because it has proven difficult to incorporate and activate sufficient acceptor concentrations in order to overcome the intrinsic n-type nature of ZnO. Indeed, native defects (O vacancies and Zn interstitials) and common background impurities (such as H, Al, and Ga) act as donors in ZnO and compensate the acceptors [20]. As an alternative to ZnO homojunctions, LEDs based on hybridization with p-GaN may profit from the ZnO exciton binding energy and the mature p-type doping know-how of GaN. Figure 12 shows a schematic of a *n*-ZnO/ *p*-GaN:Mg heterojunction LED plus the corresponding electroluminescence (EL) spectrum [21].

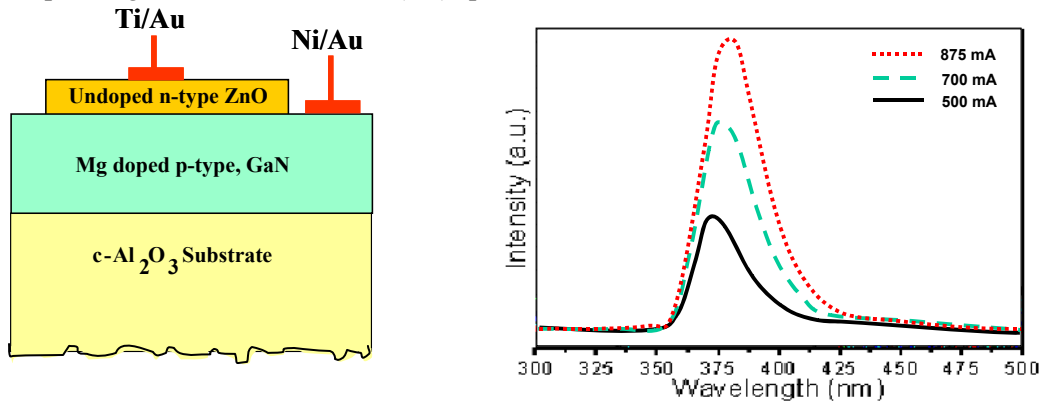


Figure 12, A schematic of the hybrid LED and the electroluminescence (EL) spectrum.

The spectrum exhibits a single peak in the near UV centred at around 375 nm. This is characteristic of Near Band Edge (NBE) emission from ZnO and indicates that there is radiative recombination in the ZnO layer. This implies that there was significant hole injection from the GaN:Mg into the ZnO and confirms that the EL in such hybrid devices may have the potential to profit from the elevated ZnO exciton binding energy.

### 3.4.3 Green Gap

AlInGaN-based LED performance is highly wavelength-dependent. In particular, the efficiency of LEDs drops off dramatically in the green: “the green gap” [22]. One of the main causes is that the elevated substrate temperature ( $T_s$ ) necessary for the *p*-GaN causes In to leak out of the active layers in the InGaN/GaN multi-quantum-wells (MQWs). This severely compromises the brightness, efficiency, and lifetime of green LEDs. Figure 13 shows a schematic of a novel LED structure we developed to tackle this problem [23].

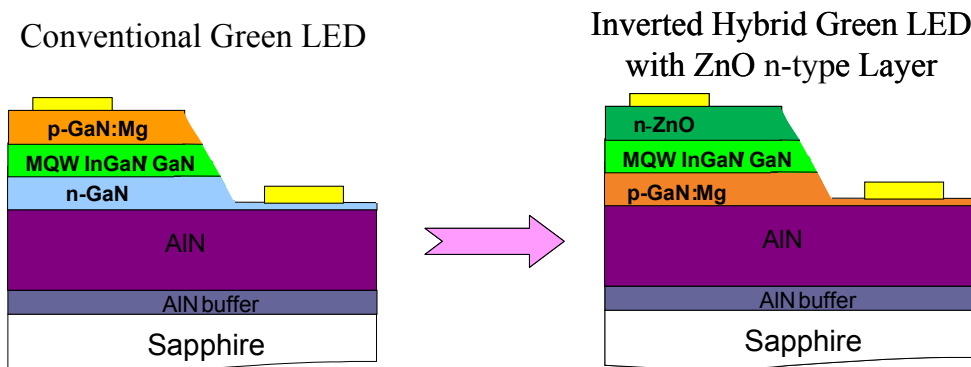


Figure 13. Schematic of inverted  $p$ - $n$  junction green LED structure with  $n$ -ZnO substituted for  $n$ -GaN.

This LED has an inverted  $p$ - $n$  structure, with  $n$ -type ZnO substituted for the  $n$ -type GaN. Through the use of PLD for the ZnO deposition, the top layer growth can be performed at significantly lower  $T_s$ . In this way, thermally induced degradation of the InGaN can be avoided and the integrity of the MQWs can be maintained. Prototype devices exhibited green EL peaked above 510 nm, as shown in Figure 14.

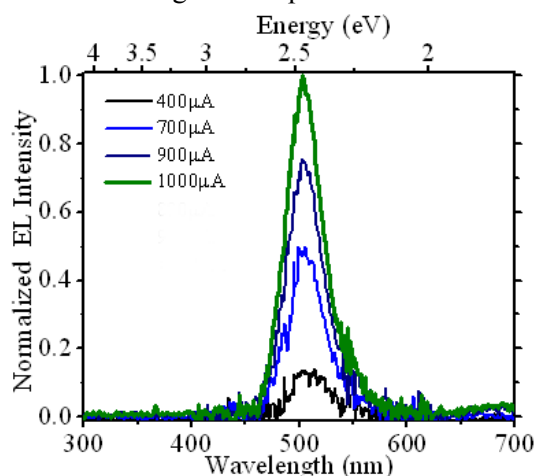


Figure 14. EL spectrum showing green emission from inverted hybrid heterojunction with PLD  $n$ -ZnO substituted for MOCVD  $n$ -GaN.

#### 4. CONCLUSIONS

This paper illustrates how ZnO-based thin films and nanostructures grown by PLD can contribute to resolve issues in some key emerging optoelectronic applications. First of all, ZnO is currently displacing ITO for many TCO applications due to recent improvements in attainable AZO conductivity combined with processing, cost and toxicity advantages. Secondly, significant advances in the mobilities and  $I_d$  on/off ratios which can be obtained with ZnO-based TFTs have opened up the potential for replacing  $a$ -Si select FETs in future AM-OLED and LCD screens. Thirdly, reflection measurements of self-forming, moth-eye-like, nanostructure arrays revealed  $<0.5\%$  reflectivity over the whole visible spectrum (for angles of incidence between 10 and 60 degrees). Such nanostructures may be useful for applications such as AR coatings on solar cells. Fourthly, PLD ZnO layers crystallise well on mismatched/amorphous substrates. Due to their similar crystal structure, such ZnO films can be used as templates for epitaxial regrowth of GaN. This approach could be used to facilitate chemical lift-off of GaN-based LEDs from insulating sapphire substrates or allow

the growth of InGaN-based solar cells on cheap substrates. Finally, LEDs based on the hybridisation of n-ZnO and p-GaN may be useful for the manufacture of UV and green LEDs. Simple n-ZnO/p-GaN heterojunction prototypes gave ZnO NBE UV EL peaked at around 375 nm. This suggests that there was significant hole injection into the ZnO and that such LEDs may profit from the relatively high exciton binding energy of ZnO. LEDs with an inverted p-n heterojunction (n-ZnO/InGaNMQW/p-GaN) were developed in order to combat the “green gap”. Low Ts PLD growth of the top n-ZnO was employed in order to maintain the integrity of the InGaN/GaN MQWs. Prototypes gave green EL peaked at just over 510 nm.

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