Large Area Multi-Wafer MOCVD of Transparent and Conducting ZnO Films

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ABSTRACT

ZnO thin films are of interest for an array of applications, including: light emitters, photovoltaics, sensors and transparent contacts, among others. Production routes for ZnO include sputtering, MBE and MOCVD. This paper focuses on our efforts to produce a large scale MOCVD thin film production tool and the results obtained from the reactor. Specifically, we have constructed a tool with a 16" wafer carrier that uniformly deposits ZnO films on 38x2" wafers simultaneously. The reactor operates at low pressure (<0.1 Atmosphere) and through 700^{o}C. High quality, uniform films have been deposited on an array of substrates. Al-doped films exhibited resistivities in the $1x10^{-3}$ ohm-cm range and transmissivity greater than 80%. Film morphology and crystallinity are a function of process parameters. The large area oxide MOCVD reactor design challenges and results are summarized. Tool performance and ZnO thin film quality are reviewed, as well as preliminary ZnO contact performance on GaN LEDs.

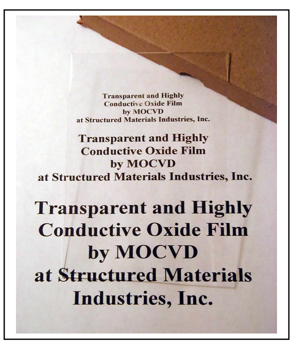
INTRODUCTION

Recently, there has been significant technical and commercial interest in GaN-based devices, due to the wide bandgap, high breakdown field and high thermal conductivity of GaN [1]. These properties enable high-power, high-frequency, and high-temperature devices, as well as high-power optoelectronic devices for use in the blue/UV wavelength range [2,3]. Light emitting diodes (LEDs) operating at blue and UV wavelengths are key components for future solid state lighting applications. The development of an efficient, high-volume production technology for high-brightness GaN LEDs will enable these products to capture a significant share of the total lighting market, which has been estimated to be over $60 billion annually [4]. The projected energy savings resulting from replacing incandescent light bulbs with high-brightness LEDs has been estimated to be $ 35 billion in the USA alone [5]. Other projected benefits include savings of natural resources and reduced emission of greenhouse gases.

A critical issue for GaN LED fabrication is the development of Ohmic contacts to p-type GaN, which optimize both the device power input and the light output [6]. Present technology uses sputtered or e beam evaporated metal films for the electrical contacts. The metal films must be made thin enough to allow for significant light extraction, which compromises power input to the device. In addition, physical vapor deposition (PVD) processes such as sputtering or evaporation result in poor step coverage, and evaporation is difficult to scale to high volume production. Sputtering may also introduce interface defects. Alternatively, transparent conductive oxides (TCOs) such as zinc oxide (ZnO) and indium-tin oxide (ITO) have high transparency at the GaN emission wavelengths, and high electrical conductivity. Using a TCO film for the contact to p-GaN allows for both maximum power input to the LED and maximum light extraction. Replacing the present PVD contact deposition processes with a metal organic chemical vapor deposition (MOCVD) process provides several additional benefits, including improved step coverage, easier scale-up to production volume and reduction of the total number of process steps.

In our own works [7], and those of others [8] the use of ITO contacts has increased light output by about 1.3 to 1.5x compared to metal contacts. The question to be answered is – can ZnO do better? ZnO has appealing properties as a contact-making material; it is: transparent, conductive, has an index of refraction of ~2.06 vs. 2.5 for GaN, may be narrowly or broadly luminescing, and is easily processed. Additionally, the ZnO MOCVD process is benign to GaN.

From our past efforts in producing ZnO films by MOCVD on substrates on wafer carriers through 300 mm diameters [9-12], we have demonstrated all the key ingredients that we believe are necessary to produce superior transparent and conductive contacts to GaN based LEDs. These properties will be briefly reviewed here. First we have shown that films can be grown on large areas (2 sheets of ~3”x5” display glass on a 300mm wafer carrier) with high transmissivity (~85 to 90%). These films were then patterned into the indicator contact for LCD displays and ultimately fabricated into displays. No difficulties were encountered with adherence. The films were simply masked and wet etched, indicating that they could easily be patterned for LEDs.



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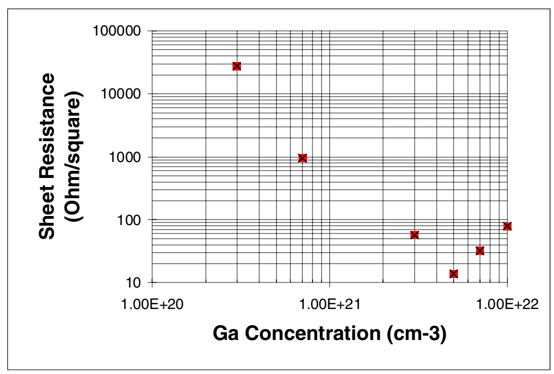

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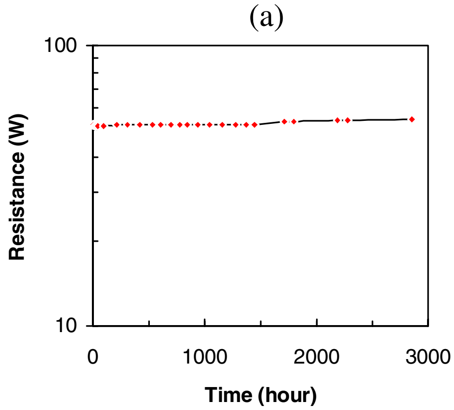

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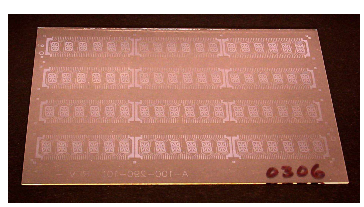


(d)

Figure 1. Thin conductive MOCVD-grown ZnO films are (a) highly transparent, typically ~85-90%, while showing great range in conductivity (b) through < 10E-3 ohm-cm, are thermally stable (c) >2000 hrs in air @ ~100C, and are easily etched as shown in the ~3”x 5” patterned display glass (d).

Other films were fabricated into transparent heaters and exhibited high stability, failing well after 2000 hours when the contact pads failed – not the film.

Another very important feature of MOCVD growth of ZnO films is that the film structure can be greatly tuned on almost any surface by changing the process parameters, as shown in Figure 2. Specifically, we have grown fully dense epitaxial or amorphous films, close packed columnar structures, porous films (not shown), and nanowires. Each of these films has different properties with respect to light emission and metal contacting.

The objective of this work has been to develop a viable production method for superior transparent conductive contacts to GaN-based p-type terminated surface-emitting LEDs. In this case viable production means uniform and repeated production of films that offer efficiency enhancements deposited at sufficient rates to meet continuous GaN LED production, without adding cost to the product.

SMI has worked with both static and high-speed rotating disc reactors. Based upon past efforts and a desire to mitigate chemical prereactions, we elected to scale the high speed rotating disc reactor for depositing ZnO over large areas. The high speed rotating disc reactor offers unique advantages in growth rate, uniformity and freedom from particulates.

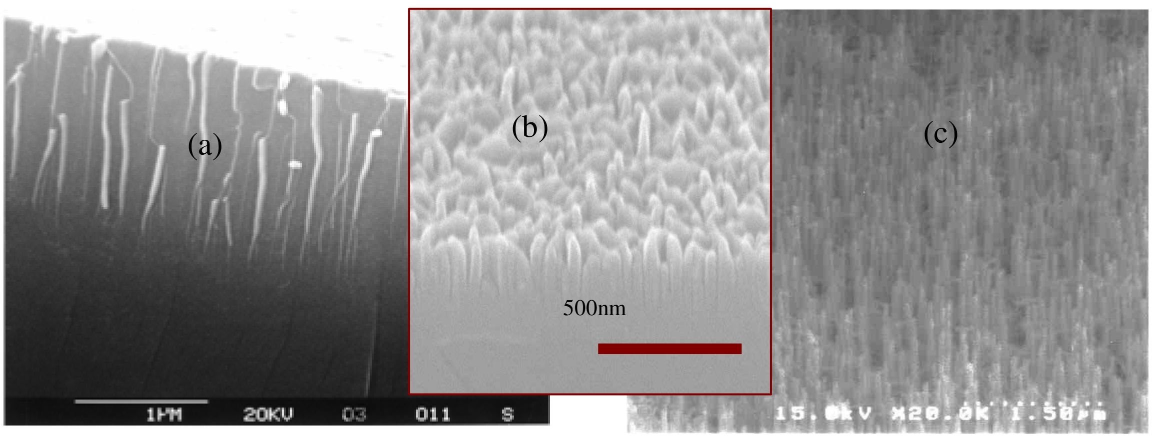


Figure 2. Example of the range of film structures that can be produced by MOCVD a) Highly crystalline continuous film, b) close packed oriented crystalline columns, and c) arrayed nanowires.

In high speed (several hundred rpm) rotating disc reactors the substrate holder is a disc in the horizontal plane in a vertically oriented reactor. The substrate holder is typically heated radiatively from below. Precursors in vapor form, along with carrier gases, are injected downwardly from the top of the reactor. Without high speed rotation, natural thermally-driven buoyancy pushes gases heated at the deposition plane upward and thus disruptively against the downward flow, which would lead to increased prereactions of the precursors and non-uniform film deposition. The high speed rotation imparts a viscous drag on the gas which literally pumps (pulls) the buoyant gases directly down to the surface, fully countering the buoyancy. The result is a laminar flow of the gases across the surface to the edge of the disc where it mixes with the general gas flow to be swept out of the system and into the exhaust as byproduct waste gases. A further innovation to the technology was the introduction of radially grading of the precursor as it is introduced within the uniform downward gas flow. This innovation counters the tendency of precursors to self-deplete as they chemically react and deposit films – without our controlled replenishment of precursors, the central region would grow non-uniformly. These innovations in MOCVD technology, combined with the engineering achievements of a uniform temperature in the deposition plane, result in highly uniform film deposition of pure, compositionally and structurally controlled electronic and optical films. Figure 3 shows the number of wafers available for different size wafer carriers. The 16” or 400mm wafer carrier offers growth on 38 50mm wafers per deposition run, which, as based upon ZnO deposition rates, should handle the output of 2 to 4 GaN LED production tools.

RESULTS:

In order to grow uniform films, a uniformly heated deposition plane is needed. We designed a special four zone heating system [13] as shown in Figure 4. Distinct effort was required to account for the high temperatures, thermal expansion and the oxidizing atmosphere. At top left in the figure is shown the filaments heated in air (an advantage of the oxidizing environment for ZnO growth is that the equipment can generally be tested in air). At lower left in Figure 4 is shown a graphite wafer carrier coated with SiC under rotation at 700 rpm heated to ~600C, again in air. Three wafers are mounted on the wafer carrier. The insert in the lower picture shows a metal wafer carrier fully populated with wafers. At right in Figure 4 is a plot of temperature uniformity across the wafer carrier at two different temperatures.

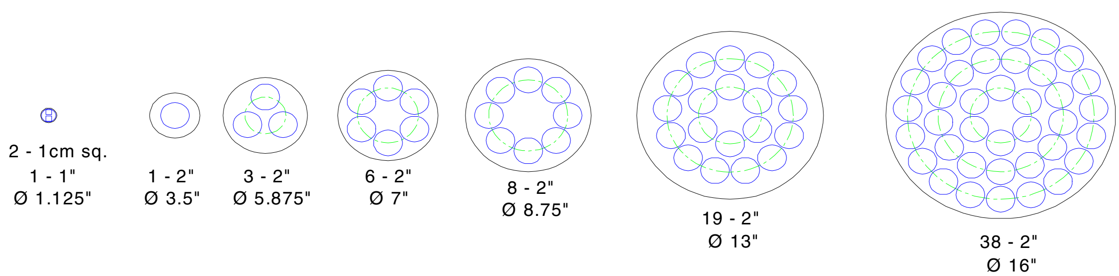
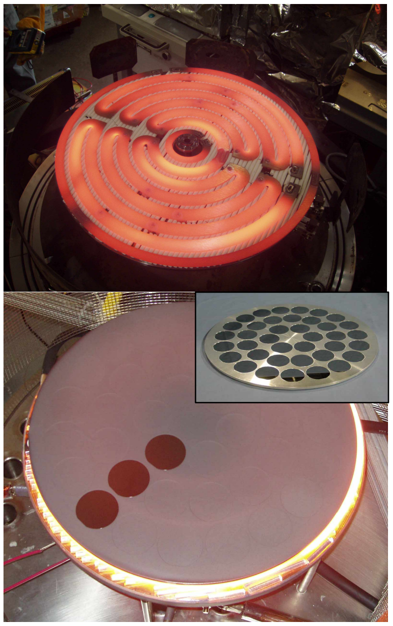


Figure 3. Wafer carriers showing scaling progression – from 25mm to 400mm.

Film depositions were initiated at ~0.05 atmospheres. Deposition temperatures ranged from 450 to 650^{o}C with gas flows on the order of 80, 15 and 200 sccm of DEZn, TMAl and O_2, which were used as the Zn, Al n-type dopant and oxidizer, respectively. Argon gas with flow ranging from 4000 to 7000 sccm was used for the inert carrier gas. A uniform downward directed flow was established into which we injected a radial distribution of the precursors. The film results are indicated in Figure 5; at top left is shown the film uniformity for wafers grown at different temperatures. Clockwise from upper center right are shown ZnO films on Si and quartz substrates. Lower right shows three Si wafers coated with ZnO on the SiC-coated platter. The overall wafer and wafer-to-wafer uniformity is <5%.

Once uniformity (few percent) and growth rates (~10 to 20 nm per minute) were established, we deposited an Al-doped ZnO film on GaN-based LED wafers with resistance less than 10E-3 ohm-cm. We further verified that the contacts made good ohmic contacts as shown in Figure 6 (left) and then proceeded to make a series of test contacts to un-patterned wafers as shown at right in Figure 6. Next the conductive films were deposited on GaN die and one to one comparisons were carried out upon devices contacted with conventional NiAu thin film metal. The results, as shown in Figure 7, were spectacular, showing a 1.7x improvement in light output over the standard NiAu contacts (~1.2x the ITO) at currents ranging from 10 to 80 mAmps. Further, the contacts also exhibited a >5x improvement upon conventional "burnout" testing.



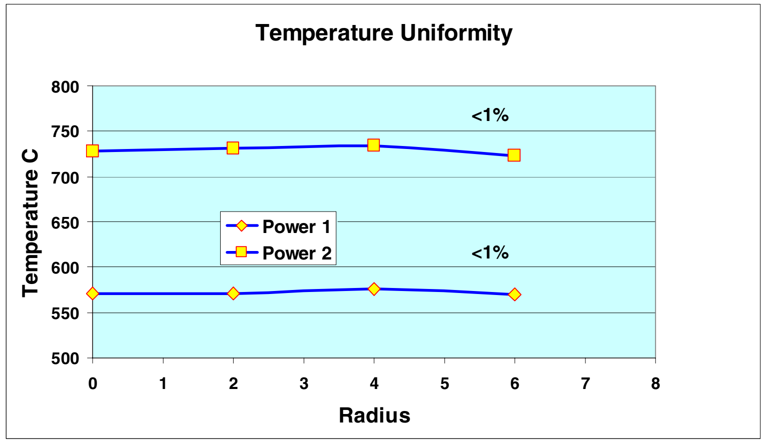
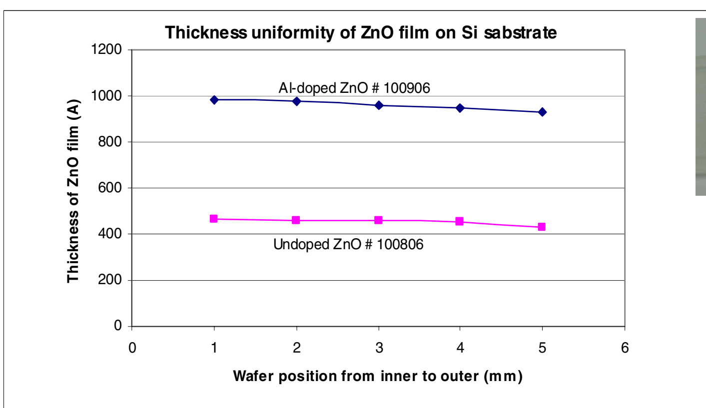


Figure 4. Top left – specially designed multi-zone filament under test in air; lower left – wafer carrier with three wafers heated at ~550C; insert shows metal wafer carrier fully populated with 2" wafers. Right – measured temperature uniformity across the wafer carrier.



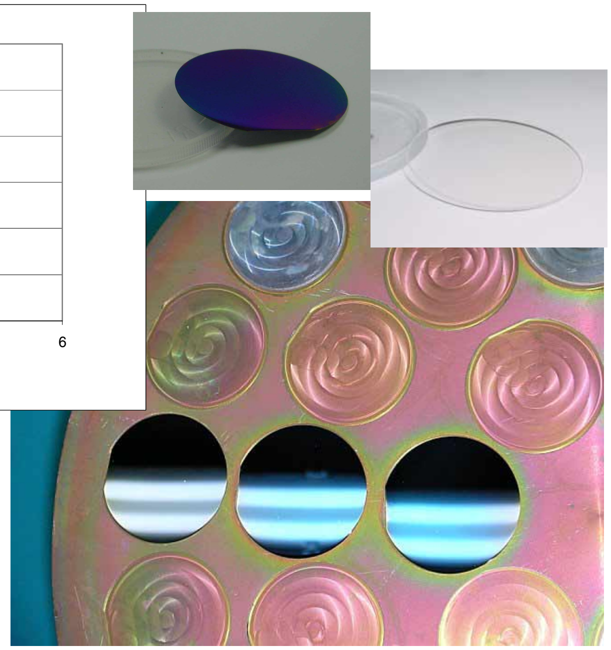


Figure 5. Top left – uniformity of ZnO film plotted for two deposition temperatures, both better than ±4%. Clockwise – images of ZnO on Si, ZnO on Quartz and three ZnO films on Si during uniformity calibration.

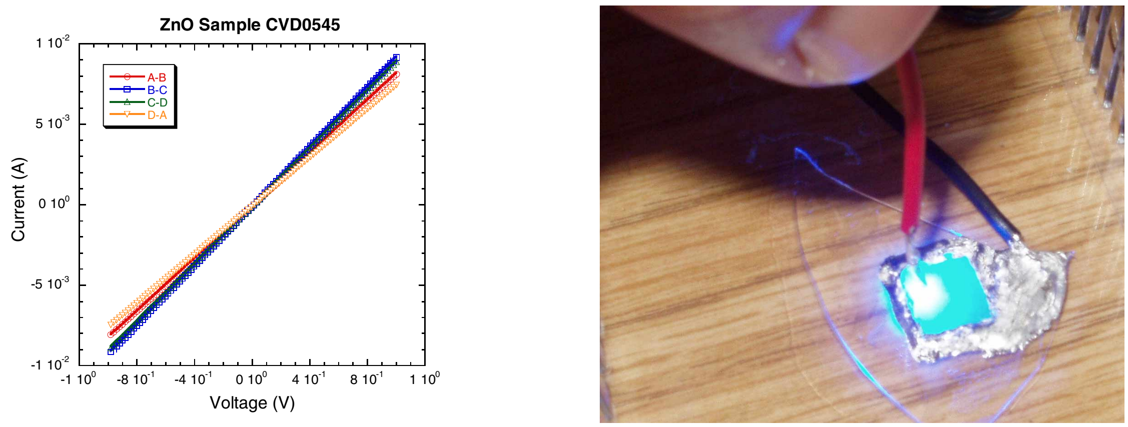


Figure 6. ZnO ohmic contact trace (left), and directly ZnO-contacted un-patterned GaN LED epi layer wafer (right).

CONCLUSIONS:

In conclusion, we have shown that a tool to grow high quality transparent and conductive ZnO films over areas large enough and at rates high enough to support their use in the production, as the contact layer, in high brightness GaN LED manufacture is viable. Further, we have shown that the produced contact is indeed superior to both metal (NiAu) and indium tin oxide (ITO) standard commercial contacts. The developed tool operates through 700 C from less than 0.07 atmospheres through to atmospheric pressure. Both deposition temperature and deposited film uniformity meets manufacturing needs. The throughput is such that one 400mm wafer carrier system depositing on 38 – 50mm wafers can support 2 to 3 equivalent GaN production tools. The film quality can be tuned, using process parameters, to yield a variety of properties optimized for specific device performance. The produced GaN contacts have yielded superior device performance, ~1.7x standard metal contacts or ~1.2x standard ITO contacts. We conclude that MOCVD is desirable for TCO contact production needs and expect that this will rapidly transition into manufacturing.

Vf ↓ 20%   Light output ↑25%

NiAu – 1x
ITO (sputtered 1.3 – 1.5x)
ZnO (MOCVD 1.7x,
~>5x fast lifetime ITO)

More Output Power – Less Heat

Table 1: Significant results of the work

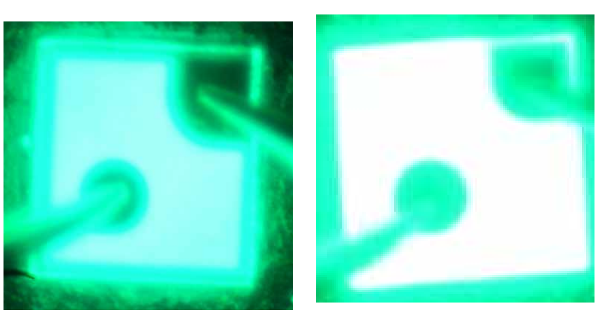


Figure 7. Comparison of GaN LED light output when standard Ni/Au contacts are used vs. ZnO contacts: (left) Light output from Ni/Au contacted GaN LED: 40 mA current, output = 190.82 mcd at λ = 509.08 nm; (right) Light output from ZnO-contacted GaN LED, 40 mA current, output = 354.58 mcd at 501.71 nm.

Lastly, looking toward the future, our results may open an even greater path for solid state lighting, because it may be important to consider the economics of the potential to integrate the TCO layer both as or with a stable phosphor. For examples, we have shown that by minor modifications to the base ZnO composition, the output of GaN LEDs can be made to vary greatly in the visible spectrum – see Figure 7; further, as seen in the insert in Figure 8, we have also shown that $ZnSiMnO_x$ can be an extremely efficient green phosphor [14]. We believe that integration of phosphors with the TCO and the LED [15] will have tremendous impact on the Solid State Lighting industry over the next several years and that the availability of MOCVD tools capable of meeting production needs will be of paramount importance to the industry over the next several years.

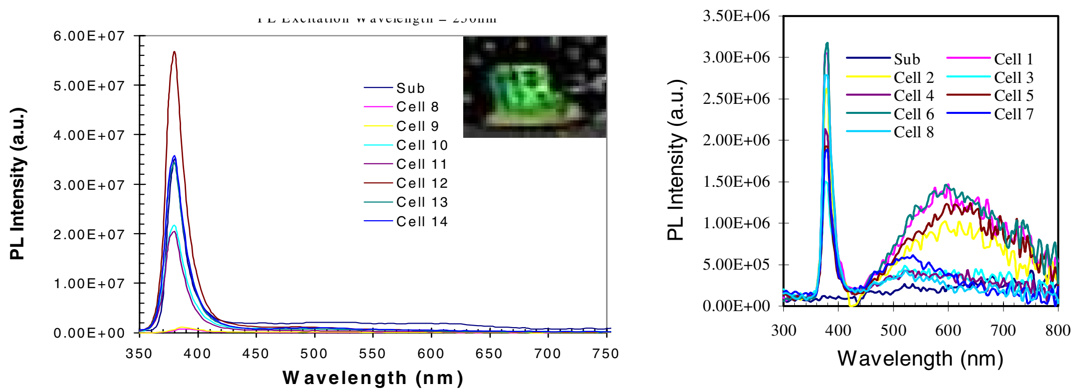


Figure 8. MOCVD-grown ZnO films, showing the narrow (left) and broad spectrum (right) photoluminescence that result from different processing conditions. The insert shows bright green electroluminescence of a MOCVD grown ZnSiO:Mn film in room light.

REFERENCES

1. S. Strite, H. Morkoç, "GaN, AlN, and InN: A review", Journal of Vacuum Science & Technology B, Vol. 10(4), p.1237 (1992).
2. F.A. Ponce and D.P. Bour, "Nitride-based semiconductors for blue and green light-emitting devices", Nature, Vol. 386, p. 351 (1997).
3. S.P. Denbaars, "Gallium-nitride-based materials for blue to ultraviolet optoelectronics devices", Proceedings of the IEEE, Vol. 85(11), p. 1740 (1997).
4. D.A. Steigerwald, J.C. Bhat, D. Collins, R.M. Fletcher and M.O. Holcomb, "Illumination With Solid State Lighting Technology", IEEE Journal Selected Topics In Quantum Electronics, Vol. 8(2), p. 310 (2002).
5. J.Y. Tsao, "Solid State Lighting", IEEE Circuits and Devices Magazine, p. 28, May/June (2004).
6. D. Steigerwald, S. Rudaz, H. Liu, R.S. Kern, W. Götz and R. Fletcher, "III-V Nitride Semiconductors for High-Performance Blue and Green Light-Emitting Devices", Journal of Metals, Vol. 49(9), p 18 (1997).
7. Unpublished work, Podium Photonics, Ltd.
8. D.S. Leem, J. Cho, C. Sone, Y. Park, and T.Y. Seong, "Light-output enhancement of GaN-based light-emitting diodes by using hole-patterned transparent indium tin oxide

electrodes", Journal of Applied Physics, Vol. 98(7), 076107 (2005).; J.H. Lim, E.J. Yang, D.K. Hwang, J.H. Yang, J.Y. Oh and S.J. Park, "Highly transparent and low resistance gallium-doped indium oxide contact to p-type GaN", Applied Physics Letters, Vol. 87(4) 042109 (2005).; J.O. Song, J.S. Kwak, Y. Park and T.Y. Seong, "Improvement of the light output of InGaN-based light-emitting diodes using Cu-doped indium oxide/indium tin oxide p-type electrodes", Applied Physics Letters, Volume 86(21) 213505 (2005). Tadatsugu Minami, Transparent conducting oxide semiconductors for transparent electrodes, Semicond. Sci. Technol. 20 (2005) S35-S44.

9. E. W. Forsythe, Y. Gao, and G. S. Tompa, *J. Vacuum Sci. Technol.* **A17** (1999) 1761.
10. G. S. Tompa, L. G. Provost, and J. D. Cuchiaro, *Proc. MRS Workshop on Transparent Conducting Oxides,* June 2000.
11. "MOCVD Zinc Oxide Films For Wide Bandgap Applications", C.E. Rice, G.S. Tompa, L.G. Provost, N. Sbrockey, J. Cuchiaro, , *Materials Research Society Symp. Proc.* **764**, C3.10.1 (2003).
12. “Metalorganic Chemical Vapor Deposition and Characterization of ZnO Materials”, S. Sun, G. Tompa, B. Hoerman, D. Look, B. Claflin, C. Rice and P. Masaun, *J. Electron. Materials*, **35**, 766 (2006).
13. “Filament support arrangement for substrate heating apparatus”, G. Tompa, priority of provisional patent filed February 11, 2006.
14. “Developing High-Efficiency Zn2SiO4:Mn Thin-Film Phosphors for Flat-Panel Cathodoluminescent Displays”, J. Liu, D. C. Morton, M. R. Miller, Y. Li, E. W. Forsythe, and G. S. Tompa, Mater. Res. Soc. Symp. Proc , pp. 305-311. (1997) and "High-Efficiency Zn2SiO4:Mn Thin-Film Phosphor for Flat-Panel FEDs", Liu, J. Morton, D. C. Miller, M. R. Krzykowski, P. F. Li, Y. Forsythe, E. W. Tompa, G. S. Bloomstein, T. M. Palmacci, S. T. Rothschild, M., SID INTERNATIONAL SYMPOSIUM DIGEST OF TECHNICAL PAPERS, 1997, VOL 28, pages 337-342.
15. “Self assembled controlled luminescent transparent Conductive Photonic Crystals for Light Devices”, G. S. Tompa, S. Sun, C. E. Rice, N. Sbrockey, and L. G. Provost, priority of provisional patent filed October 4, 2006.