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Abstract. This paper presents a compact survey of the various material schemes and device structures that have been explored in the quest toward developing light-emitting diodes (LEDs) based on zinc oxide (ZnO) and related II-oxide semiconductors. Both homojunction and heterojunction devices have been surveyed. Material for fabricating these devices has been grown with a number of different techniques, such as pulsed laser deposition, molecular beam epitaxy, metal-organic chemical vapor deposition, and atomic layer epitaxy. This review also features a self-contained introduction to materials science and device processing technologies that are relevant for fabricating ZnO LEDs. These topics include dry and wet etching, contact formation, and optical doping of ZnO. Due to the overwhelming importance of p-type doping of ZnO for making electronic and optoelectronic devices, a separate short section on electrical doping of ZnO is also included. The rest of this paper describes several different attempts at making blue- and ultraviolet-emitting ZnO LEDs. These include simple pn-junction devices as well as more complicated heterostructure devices incorporating charge carrier barriers and quantum wells. © 2019 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.OE.58.1.010901]

Keywords: zinc oxide; light-emitting diode; oxide semiconductors; semiconductor heterostructures.

Paper 181495V received Oct. 24, 2018; accepted for publication Dec. 18, 2018; published online Jan. 17, 2019.

1 Introduction

Advances in the technology of electronic and optoelectronic devices are often a result of the development of new material systems with properties that are superior to those of existing materials. This happened when silicon replaced germanium in the early years of the semiconductor industry. Another time this happened was when gallium arsenide emerged as a semiconductor of choice for building extremely fast devices. A similar development may be in the offing for optoelectronics this time with the advent of zinc oxide (ZnO). This is a promising material that might one day substantially replace gallium nitride (GaN) as the material of choice for making short-wavelength light emitters and detectors. ZnO—a II–VI oxide semiconductor—possesses properties that are broadly similar to that of GaN, which is now almost universally used for making blue light-emitting diodes (LEDs) and violet lasers, as well as a number of other devices. A number of years ago, GaN emerged as the leading material from which short-wavelength optoelectronic devices are fabricated. Its dominance has remained unchallenged so far and has only grown with further advances in the technology of III-nitrides. ZnO now appears to have the potential to challenge the pre-eminence of III-nitrides, but whether it lives up to its promise in the coming years will depend on whether the considerable challenges that remain before this material becomes industrially useful could be overcome in an acceptable manner. Mere laboratory advances will not be sufficient—robust and reliable processes will have to be developed that could be used to routinely fabricate efficient, stable, and long-lived devices on a large scale. Nevertheless, working devices have been built from ZnO and related materials that show the potential inherent in this material system.

LEDs made from ZnO have received the most attention to date and the aim of this focused review is to highlight the various approaches that have been taken in recent years to fabricate both heterojunction and homojunction ZnO LEDs. The high binding energy of excitons in ZnO, relative to thermal energy at room temperature, makes ZnO LEDs and diode lasers potentially brighter than comparable devices made from other semiconductors. This can have dramatic consequences for near- and mid-ultraviolet (UV) emitters where GaN has not performed so well in terms of cost and device efficiency. If potential problems with ZnO family semiconductors, as outlined later in this paper, could be overcome then high-brightness solid-state light sources will become possible for such budding applications as water purification, resin cross-linking, microprinting, high-density data storage, non-line-of-sight optical communication, and indoor plant growth, to name a few. However, in order to enable these advances and to open new markets, considerable work still needs to be done to perfect the art of making high-quality ZnO-based pn-junctions.

We start with a brief mention of the steadily increasing importance of solid-state lighting during recent years. This technology has been driven by the emergence of the blue-emitting GaN-based LED, but ZnO could surpass it if the technical problems associated with its controlled doping are successfully solved in the coming years. Next, we look at the material properties and device fabrication technologies that are relevant for making LEDs out of II-oxides centered on ZnO. A good understanding of these topics is essential for fabricating working ZnO LEDs. A short section that mentions the problem of p-type doping of ZnO comes next. This has remained as the central issue that has, so far, precluded the realization of commercial ZnO LEDs. After that we survey the work that has been done by several groups around the world to demonstrate working ZnO LEDs—both heterojunction and homojunction. This review ends with

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a brief end note outlining the current status of ZnO LEDs and the need for further progress in this field.

2 Solid-State Lighting with Wide Bandgap Semiconductors

Since the mid-1990s, high-power white LEDs capable of space illumination have become widely available. A radical departure from conventional means of generating light, LEDs have features that make them especially suited for lighting applications. Their small size, high efficiency in converting electrical energy to light, absence of radiated heat and UV, availability in many colors (including white), and the absence of environmentally harmful substances that might pose a problem during disposal, make them ideal as light sources for almost any conceivable illumination application.^{1,2} Little wonder that LED-based luminaires are finding increasing acceptance all over the world. From domestic light bulbs to car headlights and from projector lamps to light sources for horticulture, we now find LEDs being used in all walks of life. The market for LEDs and solid-state lighting systems has been growing at close to 25% per annum for the past several years and by all indications will continue to do so for the foreseeable future.

LEDs for space lighting applications are mostly based on blue-emitting GaN LEDs pumping a color-converting phosphor. The phosphor—usually, but not always, based on a rare-earth-doped wide bandgap insulator host—is the luminescent material that down-converts much of the blue pump light around 450 to 470 nm to longer wavelengths in the yellow and red region. The combination of this long wavelength emission with the residual (unconverted) blue light appears white to human eyes. Many advances have been made in the science and technology of phosphors for LED applications, and, as a result, today's white LEDs emit light of much superior quality than was the case just a few years ago.³ During the first few years after the appearance of LED light bulbs, their consumer acceptance was mainly limited by the inferior quality of their light output. To many users, their light appeared too cold and markedly different from that given off by incandescent lamps. The bluish hue of those early white LEDs was due to the use of cheap narrowband phosphors. This remained an issue for several years until LED manufacturers developed better LED phosphors. The new phosphors employ multiple rare-earth ions in the same host or make use of a carefully balanced mixture of different phosphors. The rich broad spectrum of white light from current generation of LEDs is making solid-state lighting proliferate in all kinds of lighting applications.^{4,5} While phosphors are undoubtedly extremely important for LEDs, the pump chip is no less important. Principally, this is because the efficiency of the pump chip determines, to a large extent, the overall energy conversion efficiency and efficacy of phosphor-converted LEDs. This is where alternative materials, such as ZnO, can play an important role.

Commercial quality, blue-emitting diodes based on III-nitride technology were first developed in Japan during the 1980s and 1990s. The early pioneering demonstrations gave rise to the entire multibillion dollar solid-state lighting industry of today. This fact was appropriately recognized when the 2014 Nobel Prize in Physics was jointly awarded to Isamu Akasaki, Hiroshi Amano, and Shuji Nakamura “for the invention of efficient blue light-emitting diodes, which

has enabled bright and energy-saving white light sources.” GaN-family semiconductors possess favorable set of properties that enable their use for making blue and UV LEDs and laser diodes. However, technology never remains still and for many years, researchers have wondered about other possible materials for generating short-wavelength visible and invisible radiation. Of the several possibilities, ZnO clearly stands out because of its many similarities to GaN as well as some superior features. Thus it is not surprising that despite continuing difficulties in ZnO technology many attempts have been made at constructing working LEDs from this material.

3 ZnO Material and Process Technology

For the purposes of this survey, it is best to begin by briefly looking at some of the salient properties of ZnO. Interest in this material for its electrical properties dates back to the 1920s when it was investigated as a possible “crystal” for making cat's whisker diodes during the early days of wireless communications. For its other applications, of course, ZnO has been known from prehistoric times; mostly as a white pigment, that to this day is the constituent of most water color palettes. The electronic properties of ZnO began to be investigated, both theoretically and experimentally, with the dawn of the semiconductor age in the late 1940s. Materials scientists and crystallographers, metallurgists and physicists, all had a go at investigating its properties. What we know today about ZnO is a result of both early and on-going explorations of the properties of this remarkable material.

3.1 Structure of ZnO

The structure of crystalline ZnO was investigated as far back as in 1935.⁶ ZnO crystallizes with the Wurtzite structure (a hexagonal crystal structure, often adopted by binary sulphides and oxides). In this crystalline form zinc ions, Zn^{2+} are found on the sites of a hexagonal close packed sublattice interpenetrated by a similar lattice populated with oxygen ions O^{2-} . The hexagonal unit cell is characterized by lattice parameters of $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$. This arrangement is such that each zinc ion is surrounded by a tetrahedron of four oxygen ions and similarly each oxygen ion is coordinated by a tetrahedron of four zinc ions (see Fig. 1). As a result of this tetrahedral coordination, ZnO has a polar character, giving rise to spontaneous electric polarization (as is also the case with GaN). The consequent piezoelectric properties of ZnO are important for understanding the behavior of ZnO-based devices as this material is even more piezoelectric than GaN. The tetrahedral coordination seen in ZnO is also an indicator of sp^3 bonding and indeed ZnO has a mixed ionic-covalent character with nearly equal contribution from each bonding type. This feature gives rise to some interesting chemical reactions that are possible with this oxide.

3.2 Properties of ZnO

As a semiconductor, ZnO is a direct bandgap II–VI oxide semiconductor with the minimum separation between the valence band and conduction band edges of 3.37 eV at room temperature. The large bandgap classifies ZnO as a wide bandgap semiconductor. The rather large bandgap results in ZnO being transparent to visible radiation and thus

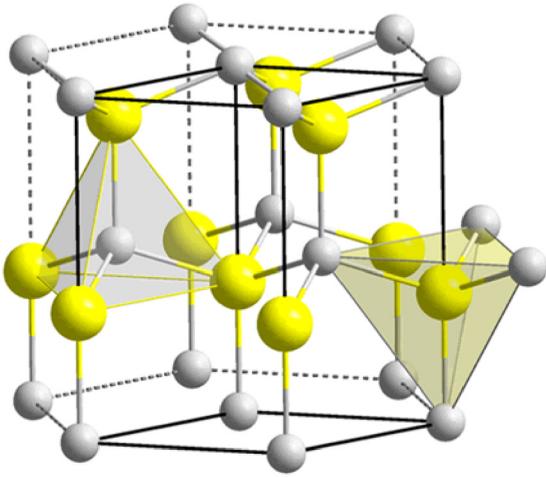


Fig. 1 Lattice structure of ZnO showing Zn^{2+} ions (yellow) and O^{2-} ions (gray).

polished single crystals of ZnO, on cursory examination, appear just like pieces of ordinary glass (see Fig. 2). The bandgap of ZnO is almost the same as that of GaN and thus these two semiconductors share many physical properties; though there are also many dissimilarities.

ZnO has certain superior attributes compared to GaN when it comes to making optoelectronic devices. To begin, ZnO is an environmentally friendly material because zinc is both plentiful in the earth's crust and is nontoxic to humans. The biocompatibility of ZnO has led to its use in many oral and topical medicines. Gallium in GaN, on the other hand, is a relatively scarce and heavy metal, which is toxic to humans. Unlike GaN, ZnO requires no special handling or disposal considerations. More importantly for device fabrication, until recently, GaN has suffered from a well-known

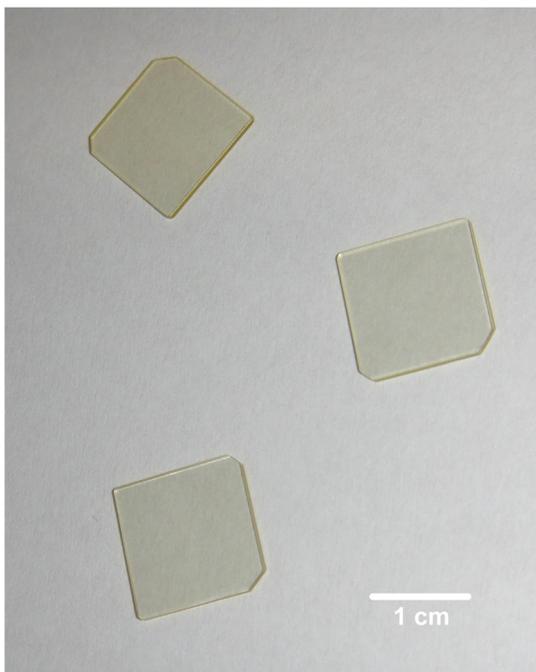


Fig. 2 Hydrothermally grown, 1 cm^2 , 2-mm thick, $\langle 0001 \rangle$ oriented, undoped ZnO wafers.

absence of bulk substrate for epitaxial growth. In the absence of a native substrate, GaN is grown on sapphire as the next best substrate material. However, the 15% lattice mismatch between GaN and sapphire results in a high density of interfacial dislocations that seriously compromise device performance. Although free-standing GaN wafers have now become available, these are currently quite expensive and are thus suitable only for making more expensive devices such as laser diodes. Bulk ZnO wafers, in comparison, have been readily available for quite some time because this material can be grown through a variety of routes, such as hydrothermal growth.^{7,8} The density of hydrothermally grown ZnO⁹ is close to 5.6 g/cm^3 , corresponding to 4.2×10^{22} ZnO units/ cm^3 . High-quality, single- and double-side polished ZnO wafers are now commercially available from several suppliers. These provide an ideal substrate for subsequent epitaxial growth, free from threading dislocations that rob GaN-based devices of much of their application potential. It is interesting to note that, due to a lattice mismatch of just 1.8% and similar chemical structures, GaN and ZnO can be epitaxially grown on each other.^{10,11} This raises the interesting possibility of combined GaN–ZnO hybrid devices and indeed most heterojunction ZnO LEDs demonstrated so far, as we shall see later in this paper, have been such hybrids.

3.3 Wet Etching of ZnO

The chemical nature of ZnO is such that it can be easily etched through wet chemical processes. While dry etch chemistries are available for ultrasmall features, where needed (such as simple CH_4 -based chemistries—see below), many devices could be fabricated by simpler wet etching processes.^{12–14} In many cases, even submicron features can be etched with acidic etchants, such as dilute orthophosphoric acid, containing appropriate surfactants. Ferric chloride and oxalic acid also work very well for etching ZnO.¹² GaN, in contrast, is very difficult to etch through wet chemistries although some attempts have been reported in the literature.^{15,16}

3.4 Dry Etching of ZnO

Good process capabilities have also been developed for dry etching of ZnO. Both chlorine-based and hydrocarbon-based dry etch chemistries for ZnO have been investigated by a number of research groups. Ip et al.¹⁷ reported results on inductively coupled plasma (ICP) dry etching of high-quality bulk single-crystal ZnO samples with both $\text{CH}_4/\text{H}_2/\text{Ar}$ and Cl_2/Ar plasmas. At low ion energies, the former gives faster etching while the latter takes over in the etch rate at higher ion energies. In the case of methane-based chemistry, low ion energies are not very effective because breaking the high bond strength of Zn–O bonds requires high-energy ion impacts. However, once the bonds are broken, ZnO can volatilize as the dimethyl zinc species: $(\text{CH}_3)_2\text{Zn}$. The high vapor pressure of this compound (301 mTorr at 20°C) is the cause of the high-ultimate etch rate seen with methane-based chemistries. On the other hand, for ZnCl_2 formed with chlorine-containing chemistries, the etch product has a lower vapor pressure of about 1 mTorr at 428°C consistent with the slower etch rates seen with this chemistry. Ip et al. also found that the near-surface stoichiometry of ZnO was unaffected by

$\text{CH}_4/\text{H}_2/\text{Ar}$ etching, as measured by Auger electron spectroscopy. That led them to conclude that the $\text{CH}_4/\text{H}_2/\text{Ar}$ plasma chemistry is capable of equirate removal of the Zn and O etch products during ICP dry etching. This ion-assisted nature of ZnO dry etching creates nice vertical side-wall profiles. Also because the near-surface stoichiometry is maintained, so the etching process produces only a small degree of surface roughening. Additional work on ICP etching of ZnO using methane-based chemistry, carried out in South Korea by Lee et al.,¹⁸ has also corroborated these findings. The effect of the inert gas used in the etching gas mixture was investigated by Lim et al.¹⁹ at the University of Florida. They found higher etch rates when using Ar or Xe than with He, which again highlights the role of effective momentum transfer in breaking the strong Zn–O bonds. While pure chlorine-based plasmas are considerably slow at etching ZnO, derived chemistries such as those based on BCl_3 have been shown to be more effective. Kim et al.²⁰ investigated ZnO etch rates as a function of $\text{BCl}_3/\text{Cl}_2/\text{Ar}$, BCl_3/Ar , and $\text{BCl}_3/\text{CH}_4/\text{H}_2$ chemistries. They found that compared with Ar, Cl_2/Ar , and CH_4/H_2 -based gas mixtures, pure BCl_3 gas results in substantially high etch rates; indicating that B and BCl radicals react with ZnO and form volatile compounds such as B_xO_y and/or species containing BCl–O bond.²¹ The oxygen is thus removed by boron, whereas zinc is removed concomitantly by chlorine, with the formation of ZnCl_2 . It should also be mentioned here that dry etching can cause both mechanical and radiation damage to most materials but ZnO is exceptionally radiation-hard and can tolerate high amounts of irradiation without significant damage.²²

3.5 ZnO as a Transparent Conductive Oxide

Heavily aluminum-doped ZnO (Al:ZnO; also referred to as AZO) is transparent and exhibits high metallic conductivity. This transparent conductive material has been well-studied²³ and could be easily integrated with ZnO-based optoelectronic devices.²⁴ AZO films can be deposited by a variety of methods, such as sol–gel techniques,²⁵ pulsed laser deposition,^{26,27} atomic layer deposition (ALD),^{28,29} and radio frequency (RF) magnetron sputtering.^{30,31} No comparable material exists within the III-nitride family. GaN devices have to make do with either indium tin oxide (ITO) or nickel-gold bilayer films where a trade-off between high optical transparency and high electrical conductivity is involved.

Superior epitaxial optoelectronic material is possible with ZnO because a ZnO light emitter can be constructed entirely from the same material system with the substrate, buffer, charge transport layers, active layers, and current spreading layers all epitaxially grown in one metal organic chemical vapor deposition (MOCVD) reactor with an integrated process flow. These both improve the material quality and reduce growth cost and complexity. No other known material system offers this kind of integration potential.

3.6 Optical Characteristics of ZnO

The refractive index of ZnO is 13% lower than that of GaN (2.05 versus 2.36). This essentially means that light can be extracted more easily from the confines of a ZnO-based light emitting device. To enhance light extraction even further, topographic photonic crystal structures can be produced on ZnO-based light emitters.^{32,33} Photonic crystal light

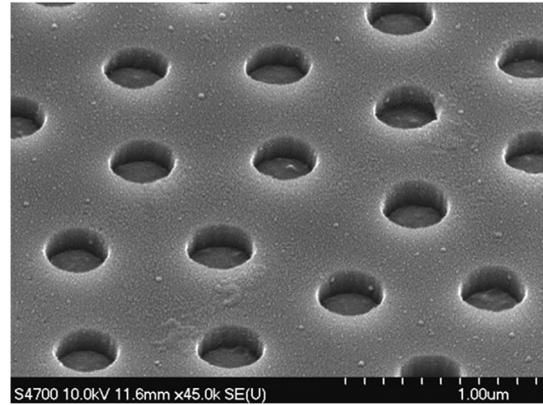


Fig. 3 Photonic crystal light extraction structure etched into the top of a GaN light-emitting device.

extraction structures on ZnO devices are shallower and easier to fabricate than those on GaN devices (see Fig. 3 for an example of photonic crystal structure on a GaN light-emitting device). This should lead to brighter devices that have a convincing external quantum efficiency advantage over GaN-based devices.

Perhaps the most often cited advantage of ZnO over GaN for making LEDs is the higher excitonic energy in the II-oxide system.^{34,35} ZnO has an exciton binding energy close to 60 meV, more than twice that of the 20- to 25-meV value for GaN. Thus light emitting devices made from ZnO should be brighter than comparable GaN-based devices at the same operating current. In other words, ZnO-based light emitters should be more efficient when compared with similar GaN-based devices. This also means that laser diodes made out of the ZnO system should have lower threshold current requirement when compared with GaN-based laser diodes.

3.7 Electrical Contacts to ZnO

Good electrical contacts are essential to the functioning of all electronic and optoelectronic devices. Contact technology for ZnO family materials has made considerable progress in recent years.^{36,37} Various metallization schemes have been reported for n- and p-type contacts to ZnO. As expected, n-type contacts exhibit lower specific contact resistance compared to p-type contacts. Various wet³⁸ and plasma-based dry^{39,40} contact pretreatment procedures have also been reported to reduce specific contact resistance to ZnO.

3.8 Some Shortcomings of ZnO as an Optoelectronic Material

Together with all these advantages, ZnO also has some features that are not as attractive for making light-emitting devices. For one, ZnO is considerably softer than GaN and is more easily attacked by a variety of chemicals, making it a less robust material. Then ZnO is also thermodynamically less stable than GaN and related compounds. This is easily observed when a sample of ZnO turns yellow on heating—a strong thermochromic effect due to the formation of *in situ* oxygen ion vacancies. Furthermore, ZnO is also much harder to dope with optically active ions, such as the rare earths. GaN, in contrast, is easy to dope with both transition metal and rare-earth ions.^{41,42} Lanthanide-doped GaN material is now slowly emerging as an interesting alternative for making

GaN-based color LEDs;^{43,44} doing the same with ZnO may not be possible or will require further research effort. However, most importantly, the biggest single reason for the lack of progress with ZnO devices has been the inability to create robust p-type material. The following section takes a look at this continuing problem.

4 Electrical Doping of ZnO

Synthetic, as-grown ZnO exhibits n-type conductivity. The origin of this is not definitively established yet but, principally, it appears to be due to a large number of native defects, such as oxygen vacancies, zinc vacancies, oxygen interstitials, and zinc interstitials.⁴⁵⁻⁴⁷ Of these, oxygen vacancies have the lowest formation energy and are thus the easiest to form.⁴⁸ This feature makes it difficult to induce significant amount of p-type character through known doping techniques. The major remaining problem with ZnO has been the unavailability of sufficiently highly doped p-type material. This problem is also seen with other III-V and II-VI wide bandgap semiconductors—almost all of which are easy to dope n-type but much harder to dope p-type. In this respect, the only major exception appears to be ZnTe, which is quite easy to dope p-type.⁴⁹ However, to fabricate efficient bipolar devices, both n- and p-type materials are necessary. This has required a large amount of effort, directed toward understanding the dynamics of carrier doping in ZnO. Over the past few years, considerable progress has been made in this area and now material with hole concentration in excess of $3 \times 10^{19} \text{ cm}^{-3}$ has been demonstrated. However, the various processes developed so far have either suffered from lack of reproducibility, low achievable hole concentration, and/or gradual diminution of p-type character over time. Undoubtedly, further advances are needed in this direction so that controllably doped p-type material of reasonably high hole concentration and mobility becomes routinely available.

A good review of the general aspects of ZnO doping, bandgap engineering, and associated topics has recently been provided by Kozuka et al.⁵⁰ This review can be consulted as a starting point for understanding the contemporary material challenges with ZnO family materials. Most work on developing good quality p-type ZnO begins from assumptions that the difficulty in creating stable high hole concentration ZnO is related to either the acceptor levels being too deep, compensation of native defect levels or the low solubility of dopants.⁵¹⁻⁵³ Various research groups have then attempted to solve each of these problems in a different way.

Substitution of group-I elements for Zn sites or the substitution of group-V elements for O sites can, in principle, lead to p-type ZnO but studies, both theoretical and experimental, have shown that the situation for ZnO doping is much more complicated than, e.g., for silicon. The relative sizes of substituting ions, charge compensation effects, defect complexes, and bond strains all play important roles in the case of p-type ZnO doping and make obtaining good quality p-ZnO very difficult. A number of techniques, including secondary ion mass spectroscopy,⁵⁴ have been used for investigating the solubility, placement, and activation of a range of potential dopants in ZnO. Nitrogen-doped ZnO once appeared very promising for creating p-type ZnO epilayers,^{55,56} but it was found that N-doped ZnO is not stable at higher temperatures and also suffers from limited

dopant solubility. Similar problems have beset numerous other efforts to prepare acceptable p-type ZnO films. However, recently, Reynolds et al.⁵⁷ have shown that sufficiently high nitrogen doping followed by appropriate thermal annealing can lead to significantly high ($\sim 10^{18} \text{ cm}^{-3}$) p-type behavior in ZnO, at room temperature. Through secondary ion mass spectrometry, Raman-scattering, photoluminescence (PL), and Hall-effect studies, they concluded that the observed p-type electrical activity is a result of doped N atoms evolving from their initial incorporation on Zn sites to a final shallow acceptor complex $V_{\text{Zn}} - \text{N}_\text{O} - \text{H}^+$, with an ionization energy of around 130 meV. This complex, they determined, is responsible for the p-type character of ZnO thus doped. It should be mentioned here that very recent work has also reported on ferromagnetism in N-doped ZnO thin films,⁵⁸ which may have interesting implications for future magneto-optic devices.

Further work is proceeding on finding the best route for p-type doping of ZnO, which is stable and reproducible. An industrially acceptable method of producing p-type regions for ZnO-based devices is still not firmly established. Nevertheless, efforts continue to investigate mechanisms that seem to prevent p-type doping of ZnO as well as to find novel, ingenious methods for achieving device-quality p-ZnO material.

5 Heterojunction ZnO LEDs

ZnO can be epitaxially grown on all three common substrate materials used for making conventional blue LEDs: sapphire,^{59,60} GaN,⁶¹ and SiC.⁶² Indeed, ZnO growth on all of these substrates has been extensively reported in the literature. This trend is easy to understand as GaN-based blue LEDs—the archetypical wide bandgap LEDs—have been conventionally made through epitaxial growth on exactly these substrates. The lattice mismatch of ZnO with each of these materials is given in Table 1 here. The ability to create such heterointerfaces has been exploited in constructing heterojunction ZnO LEDs. It should be noted here that these structures should strictly be called heteroepitaxial but the term heterojunction, in this context, is common in the literature and thus this term is used throughout in this review. As mentioned before, this has been the principal way through which the unavailability of good p-type ZnO has been accommodated for making ZnO-based pn-junction LEDs. II-oxide/III-nitride heterostructures family can cover a wide space of interfacial lattice matches and band gaps. From MgZnO to CdZnO and from AlGaIn to InGaIn, a full

Table 1 Material properties of some possible substrates for the growth of epitaxial ZnO layers.

Substrates	Bandgap (eV)	Density (g/cm ³)	Lattice constant (Å)	Lattice constant mismatch with ZnO (%)
ZnO	3.4	5.6	3.25	0
Sapphire	9.1	4	4.76	46.5
GaN	3.4	6.15	3.19	1.8
Silicon carbide	3.0	3.2	3.10	4.6

range of alloy compositions are available for close across-the-interface lattice matching and bandgap adjustment. Bulashevich et al.^{63,64} have analyzed the operation of ZnO/GaN heterostructure diodes through simulations. Their studies shed light on the mechanism of operation of such heterostructure LEDs and laser diodes. Among the parameters they studied were the internal quantum efficiency of hybrid diodes and its dependence on operating temperature. A more recent review on ZnO/MgZnO heterostructures for LEDs and other optoelectronic applications has been provided by Kozuka et al.,⁵⁰ where various topics ranging from growth techniques and band alignments to device fabrication and characterization have been discussed.

Epitaxial heterostructure LED structures involving ZnO are actually easier to grow and are more forgiving in terms of lattice mismatch than is the case with III–V homo-junction LEDs.⁶⁵ This is because of the ionic character of ZnO. Ionic bonds have spherical potential wells, in contrast to the anisotropic wells of covalently bonded semiconductors. This feature makes the potential energy profile relatively insensitive to the variation of the atomic arrangement in ionic compounds compared with that in covalent compounds. Thus the interface in heteroepitaxial systems with large lattice misfits is smoothly connected in ionic materials and the formation of dangling bonds and dislocations is suppressed compared with that in covalent materials. This structural property has led to many successful demonstrations of heterostructure ZnO LEDs.

5.1 ZnO-on-GaN Heterostructure LEDs

Diodes made from n-type epitaxial ZnO overlayers grown on p-type epitaxial GaN layers have been the most studied configuration for heterojunction ZnO LEDs. The reverse structure, comprising of p-type GaN overlayers deposited on n-type ZnO, has also been investigated but its descriptions have been less common. In the case of ZnO-on-GaN structures, the GaN layer can be deposited on a variety of metamorphic substrates of which epitaxial GaN templates on sapphire substrates are the most common. An example of this kind of work was reported by a group of Russian researchers in 2003.^{66,67} They grew GaN layers through molecular beam epitaxy (MBE) on a sapphire substrate where the top layer was an Mg-doped p-type layer. On top of it, they deposited a layer of Ga-doped n-type ZnO through low-pressure chemical vapor deposition (CVD). While a variety of dopants, such as Al, can be used for preparing n-type ZnO, use of Ga is convenient in such situations as it is already present in the growth system as a component for depositing GaN. Substitutional Ga atoms on Zn sites act as n-type dopants with activation energy of around 50 meV.⁶⁸ As an illustration of material properties typically achieved with these kinds of growth processes, they measured room temperature hole density and mobility in their p-GaN to be $p = 3.5 \times 10^{17} \text{ cm}^{-3}$ and $\mu_p = 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. They also found electron density and mobility in their n-ZnO to be $n = 4.5 \times 10^{18} \text{ cm}^{-3}$ and $\mu_n = 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Diodes made from this heterostructure showed distinct pn-junction diode-like characteristics with a forward voltage of only 3 V. Electroluminescence (EL) was observed under forward bias with the intensity increasing linearly for forward currents up to 10 mA. The violet-blue light emission had a spectral peak at 430 nm with full-width at

half-maximum of about 50 nm. Cathodoluminescence (CL) studies supported the conclusion that the EL was generated in the GaN epilayer rather than in ZnO. The light was emitted when electrons injected from n-type ZnO into p-type GaN recombined with holes there. n-ZnO-on-p-GaN LEDs have recently also been made through the ALD technique.⁶⁹ Compared to MBE and MOCVD processes, ALD is still a relatively immature technology but holds great promise for structures that require the growth of extremely thin layers with very closely controlled stoichiometry. As ALD gets developed further, it will partially replace MBE and MOCVD for making ZnO LEDs because of its ability to precisely target material thickness and composition in quantum well-based devices.

Yet another work from Russia, also reported in the year 2003, described the fabrication of n-ZnO/p-AlGaIn heterostructure grown on 6H-SiC substrate.⁷⁰ In this work, the p-AlGaIn layer was grown on SiC by hydride vapor phase epitaxy, whereas the n-ZnO layer was subsequently deposited by CVD. The use of different growth techniques for growing the p- and n-type layers for such heterostructures has been a common practice. The ZnO/AlGaIn heterostructures exhibited good diode characteristics with forward voltage of 3.2 V. Above this voltage, UV light with peak wavelength of 398 nm was emitted by the diode. On raising the temperature, light emission was seen at temperatures as high as 500 K. CL studies and temperature dependence of EL supported the conclusion that the light was emitted by excitonic decay in the ZnO layer. This was one of the first demonstrations of UV emission from a heterostructure ZnO LED. Note that in this work SiC wafers were used only as the growth substrate—not as an electrically active material.

5.2 ZnO-on-SiC Heterostructure LEDs

n-type ZnO can also be directly deposited on p-type SiC to form pn-junction devices. Such a material combination was reported by Yuen et al.⁷¹ from the Nanyang Technological University in Singapore. A remarkable feature of their work was the low temperature ($\sim 150^\circ\text{C}$), in which ZnO deposition was carried out. p-doped 4H-SiC wafer with hole concentration of $1 \times 10^{19} \text{ cm}^{-3}$ and hole mobility of $120 \text{ cm}^2/\text{Vs}$ was used in this work. An overlayer of Al-doped ZnO was deposited by filtered cathodic vacuum arc technique using a ZnO target containing 3% of Al. An oxygen partial pressure of 5×10^{-4} Torr was maintained during the reactive deposition process. LEDs were fabricated from the heterostructure material and exhibited emission at 385 nm.

In yet another work pairing ZnO with SiC, a Korean team reported the fabrication of ZnO heterostructure LEDs by depositing ZnO on a SiC substrate.⁷² In contrast to other similar work, their approach involved using n-type 6H-SiC substrate, in which a 400-nm-thick Cu-doped, p-type ZnO layer was deposited by plasma-assisted MBE. This work is notable as one of the early attempts at using p- instead of n-type ZnO for making heterostructures ZnO LEDs. Introduction of Cu leads to acceptor states in ZnO located at 0.17 eV below the bottom of the conduction band, as the Cu atoms substitute for Zn atoms.⁷³

The epitaxy of ZnO with GaN can be improved by making use of the various alloying opportunities available with both systems. This will allow better lattice matching and thus reduced interfacial and threading defects as well as

the possibility of bandgap engineering for emission wavelength tuning. These considerations are even more important for fabricating UV LEDs because they have less tolerance for defects and other imperfections. A US-Taiwan team described a UV LED structure made from n-ZnMgO/n-ZnO/p-AlGaIn/p-GaN structure.^{74,75} They grew the entire structure through RF plasma-assisted MBE on c-plane sapphire templates. LEDs of conventional design were fabricated using both wet and dry etching processes, in keeping with the presence of both ZnO and GaN family layers in the heterostructure. EL, associated with ZnO excitonic transitions, was observed up to a temperature of 370°C. This work is a clear indication of the great potential inherent in ZnO for making bright high-efficiency LEDs and even lasers operating in the blue, violet, and UV regions of the electromagnetic spectrum. In an even more recent work, Kong et al.⁷⁶ inserted a 100-nm MgZnO/ZnO/MgZnO well between Ga-doped ZnO and Sb-doped ZnO layers. LEDs made from this heterostructure showed strong UV EL at injection currents ranging from 40 to 80 mA at room temperature. The output optical power was 7.3 times that from a pn-homojunction diode at the same driving current. This demonstrates good confinement of electrons and holes in the intrinsic ZnO layer of the heterostructure.

5.3 ZnO-on-Si Heterostructure LEDs

Although we have mainly reviewed work using sapphire, GaN, or SiC as substrate material, there have even been attempts to grow ZnO on silicon substrates. Given the success in growing device-quality GaN on Si for making LEDs, this is an area where we will see more activity in the future. The challenges here are similar to those encountered in GaN-on-Si epitaxy. One research group has even reported optically pumped lasing from an MOCVD-grown ZnO – on – SiO₂ disc laser.⁷⁷ As far as LEDs are concerned, Baltakesmez et al.⁷⁸ have reported on heterojunctions formed by n-ZnO thin films deposited on (100) p-Si:B using an electrochemical deposition technique. They observed broad luminescence centered at the wavelengths of 390 and 510 nm although the EL was not very strong. This is not surprising because the epitaxy of GaN-on-Si system is also very difficult and if not carried out properly usually leads to material, which is not very useful for device fabrication. However, just as the GaN-on-Si epitaxy has been mastered such that commercial LEDs are now available, it is conceivable that high-quality ZnO-on-Si material may also become available one day. Another yet-to-be-explored possibility is the growth of n-ZnO layers on commercially available GaN-on-Si wafers. This approach is now feasible as GaN/InGaN LEDs fabricated on GaN-on-Si wafers are now commercially available from companies, such as Plessey Semiconductors in the UK.

5.4 GaN-on-ZnO Heterostructure LEDs

While most ZnO/III-nitride heterostructures have been made by depositing ZnO on a nitride epilayer, growth of nitride on ZnO surfaces has also been investigated by several groups.^{11,79,80} One such work was described in 2004 by an academic–industry collaboration consisting of researchers from Virginia Commonwealth University and Cermet Inc.⁸¹ Polished ZnO wafers were first annealed at 1050°C to obtain atomically flat surfaces suitable for MBE. Studies have revealed that such thermal annealing is useful for removing

both chemical mechanical planarization damage and chemically induced damage; leaving an atomically flat face. GaN was then grown by MBE using an RF-N₂ plasma source at the rate of 300 nm/h. Alternatively, they also tried using ammonia as a source of nitrogen but found that GaN grown with ammonia was always rougher than GaN grown with nitrogen. Atomic force microscopy and PL characterizations showed that high-quality GaN epilayers suitable for device fabrication were achieved. Polarization control of ZnO epilayers grown on GaN substrates can yield high-quality UV LED material. For instance, oxygen-polar ZnO films can be grown on nitrogen-polar p-GaN-on-sapphire substrates through photoassisted MOCVD. Very recently, it has been shown that this leads to the presence of a polarization-induced inversion layer at the ZnO side of the heterojunction interface.⁸² This structure makes it possible to obtain relatively narrow band UV emitters that emit at 385 nm. Thus it seems that just as with GaN LEDs, ZnO LEDs also can benefit from proper interfacial polarization engineering. This possibility makes the GaN-on-ZnO scheme of particular interest for making ZnO LEDs.

An interesting variation on the GaN/ZnO heterostructure approach has been described by a Taiwanese team from the National Taiwan University.⁸³ What sets their work apart is their use of very thin SiO₂ layers on either side of an undoped ZnO layer. The SiO₂-sandwiched ZnO layer was sitting atop an Mg-doped p-type epitaxial GaN film on sapphire substrate. There was a Ga-doped n-type ZnO layer deposited at the top of the device to serve as the negative contact (see the device structure in Fig. 4).

Both the SiO₂ layers and the ZnO layers were deposited by RF magnetron sputtering. The silica layers were intended to serve as carrier confinement layers with carriers either tunneling through or hopping over the barriers at significant drive currents (see Fig. 5). The investigators noticed a significant decrease of defect-induced emission and enhancement of ZnO band-edge excitonic emission, compared to devices without SiO₂ barrier layers. However, their devices exhibited soft turn on characteristics and a large resistance due to the presence of barrier layers.

More recently, LEDs fabricated from a similar structure through pulsed laser deposition but without silica barrier

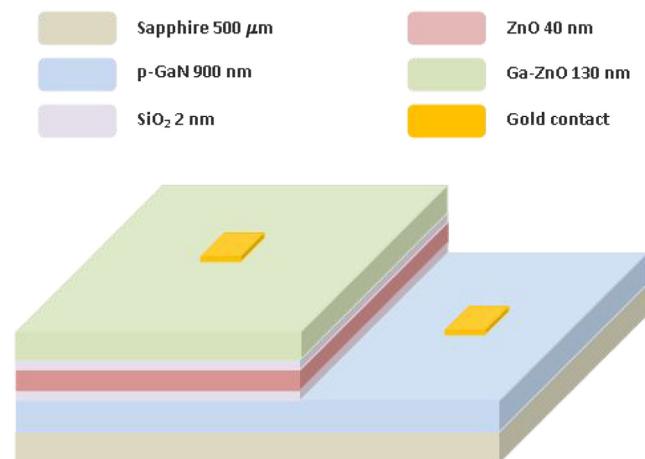


Fig. 4 Device and layer structure of a ZnO LED with silicon dioxide barrier layers.

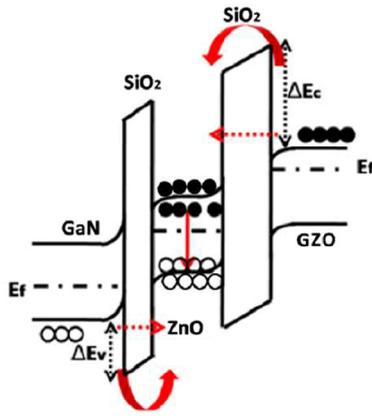


Fig. 5 Band structure of a ZnO LED with silicon dioxide barrier layers. Reprinted with permission from Ref. 83, Optical Society of America.

layers have also been described by a Chinese Inter-University collaboration.⁸⁴

In making heterostructure LEDs where ZnO is one component of the diode, materials are almost always deposited on each other through an epitaxial process. This is essential if one wants an intimate enough interface for charge carrier injection. If this is not a requirement then other methods, such as wafer bonding can be utilized. As an example of this, a wafer bonding process for making LEDs was described in 2007 by a University of California at Santa Barbara team.⁸⁵ In their work, they made use of a conventional GaN/InGaN LED wafer, which was bonded to an n-type hydrothermally grown bulk wafer. The bonding process was carried out by heating ZnO and GaN LED wafers together at 700°C in a nitrogen atmosphere under 2 MPa pressure. Heat-and-pressure wafer bonding causes some material diffusion across the bonded interface so that the interface becomes somewhat diffused but the bonded composite wafer exhibits high mechanical strength. The bonded wafers were etched to form truncated hexagonal ZnO pyramids. These served to enhance light extraction from the underlying conventional GaN/InGaN LED by reducing the refractive index discontinuity from GaN to air. They demonstrated a highly efficient “mega-cone” LED. For instance, at 50 mA forward current, their LED was 2.6 times brighter than a conventional planar GaN LED. There have been other reports^{86–89} of ZnO being used in this index-matching role with GaN LEDs, especially because it can be doped n-type easily and can thus serve as the n-type contact to the LED.

5.5 ZnO Nanowire Heterostructure LEDs

So far, we have looked at heterostructure ZnO LEDs employing planar ZnO films. Due to its morphology and growth characteristics, ZnO lends itself, under suitable conditions, to columnar growth, forming ZnO nanowires.⁹⁰ MBE, MOCVD, or hydrothermal growth can be used to grow ZnO nanowires. Semiconductor nanowires have attracted increasing attention in recent years for making light-emitting devices. When used in LEDs, nanoscale columnar morphology offers several advantages over planar films. These include increased junction area, reduced temperature sensitivity, enhanced polarization dependence of reflectivity, and improved carrier confinement in one-dimensional

(1-D) nanostructures.^{91,92} Several groups have reported fabrication of heterostructure ZnO nanowire LED structure. Park and Yi⁹³ described the fabrication of LEDs from ZnO nanowires grown on p-GaN surface (on sapphire) through catalyst-free MOCVD. They planarized the top of ZnO nanorods by impregnating and filling the nanorods assembly with photoresist. Ti/Au contact was deposited at the top end of ZnO nanorods to form the cathode contact, whereas Pt/Au contact was deposited on the p-GaN to form the anode contact. The diode thus formed showed no EL under forward bias but light emission was observed under reverse bias. At reverse voltages up to 4 V, only a broad yellow defect band luminescence was seen, but at voltages above 4 V a blue emission centered at 430 nm was also observed. Further increase of the reverse voltage to values above 6 V showed the emergence of weak UV emission. Clearly different charge injection and recombination mechanisms were being activated at different threshold voltages. Impact ionization is often the mechanism that leads to light emission in such devices. Although their device was not a satisfactory UV-emitter, it was a forerunner to other ZnO nanorods-devices that were developed later.

ZnO nanowire structures made further progress when the technology to transition from 1-D to two-dimensional (2-D) growth (or vice versa) during MOCVD growth was developed. This allows low-defect transitions between planar (2-D) and nanowire (1-D) layers. An example of this comes from a South Korean collaboration who described pn-junction diodes made by growing ZnO nanowires on p-GaN.⁹⁴ MOCVD was used to first grow a p-GaN layer on a sapphire substrate and then diethyl zinc + oxygen precursors were used to grow vertically aligned ZnO nanowires on top of the GaN layer. Growth temperature was then altered to make a transition and grow a cap layer of planar ZnO on top of the nanowire layer. Electrical contacts were deposited on the ZnO cap layer and on the p-GaN layer (exposed through etching). In structures like these, the transition between 1-D and 2-D growth is affected by changing the growth temperature and thus the diameter and density of the ZnO nanorods are dependent on the substrate temperature. Reactor pressure also influences growth morphology, as reduced pressure promotes vertical alignment of nanorods. pn-junction diodes fabricated from this material showed good rectifying behavior but a rather large forward voltage drop of around 11 V and no light emission was reported. This was attributed to interface defects and insufficient ohmic contact area. This observation underscores the fact that exquisite morphology control is essential for growing structures where a dimensional transition takes place. As this is difficult to do in a research setting, let alone in a manufacturing environment, devices with such structures are unlikely to be commercialized any time soon.

The growth of ZnO nanowires has rapidly advanced during the past decade so that higher quality material can now be grown.⁹⁵ Due to these developments, several groups have now succeeded in developing light-emitting pn-junction diodes from the p-GaN/n-ZnO nanowire system. One such work has been described by Zhang et al.⁹⁶ They grew uniform arrays of 100 to 150 nm diameter, ~5-μm long, n-type ZnO wires on p-GaN-on-sapphire substrates through a physical vapor deposition process.^{97,98} Their nanowires grew abruptly on the GaN surface without any planar ZnO layer

first forming on GaN. This resulted in an abrupt pn-junction at the GaN/ZnO nanowire interface. Weak EL was observed under a forward bias higher than 10 V. On increasing the forward voltage, the emission intensity was seen to increase and shift to shorter wavelengths. In the range of 10 to 35 V, the peak emission wavelength changed from blue (440 nm) to deep violet (400 nm). The authors proposed an interfacial band bending model to explain this observed blue shift of the EL spectrum. This model suggests that electrons from ZnO get injected into GaN where they recombine with holes to produce emission at the bandgap of GaN, whereas holes from GaN get injected into ZnO, producing emission corresponding to the bandgap of ZnO. These emissions, combined with interfacial recombination emission, lead to broadening of the emission spectrum.

In a similar work, reported by Lai et al.⁹⁹ from UC Berkeley, California, ZnO nanowire arrays grown on p-type GaN epitaxial film through a simple low-temperature solution method were used to make LEDs. Their device showed good electrical and optical characteristics with distinct blue emission at around 400 nm. However, they showed that this emission originated from radiative recombination in GaN rather than in ZnO nanowires. This highlights the fact that in heterostructure LEDs the emission can originate in either of the two layers on each side of the heterointerface or can have contributions from both. In order to obtain emission from ZnO, it is essential to perform good interface engineering to ensure that carriers of the right sign will flow in the desired direction. To confirm which material (ZnO or GaN) is the source of observed luminescence, the common practice is to investigate the PL of both ZnO and GaN material layers separately. The PL peaks for each case are then compared with the EL peak to ascertain the material that gives rise to light emission.

Clear UV emission from ZnO nanorod LEDs was demonstrated by Dong et al.¹⁰⁰ in research reported from the Institute of Semiconductors in Beijing, China. Their device was made by the hydrothermal growth of ZnO nanorods on a p-GaN layer and was completed by depositing an ITO layer at the top to serve as the cathode of the LED. The device showed strong UV emission at 390 nm. Moreover, they demonstrated that LEDs made from 300-nm diameter nanorods were brighter than those made from 500-nm diameter nanorods. This was attributed to better waveguiding properties exhibited by narrower nanorods. The same group also reported a modification of their device where instead of ITO, a layer of graphene was used as the current spreading layer of the LED.¹⁰¹ In their paper, they describe an interesting technique for transferring CVD-grown graphene from a Cu foil on to the top of ZnO nanorods. Being transparent and highly conductive, graphene films can form very good top contacts for many types of LEDs. A hydrothermal growth technique for ZnO nanorod growth has also been described by Rout and Rao.¹⁰² They grew ZnO nanorods on both p-Si and p-PEDOT:PSS substrates and fabricated LEDs from them. Their devices showed good rectifying characteristics and UV emission at 390 nm, but they also observed prominent defect-related visible light emission in the yellow-green region.

Nanowire ZnO LEDs continue to receive much attention because of their ability for better carrier confinement as compared to planar devices and for this reason they have also

been widely investigated for making GaN LEDs. In a recent work, reported by researchers from Henan University in China, a ZnO heterojunction LED, entirely comprised of single nanowires with both p- and n-type regions, was described.¹⁰³ First, CVD was carried out on Si(010) substrate to grow vertically aligned p-type AlGaIn nanowires.^{104,105} These nanowires had diameters of 100 to 500 nm and their lengths were in the range of 0.8 to 1.5 μm . Using another chemical vapor mediated process, extensions of n-type ZnO were grown as continuation of these nanowires. High resolution transmission electron microscopy showed that the AlGaIn/ZnO interfaces were very sharp and uniform with a transition region of no more than 1 nm along the wire. Thus each nanowire was essentially a single-crystal pn-heterojunction. Au/Ti bilayer metal contacts were made to the AlGaIn and ZnO ends of nanowires. Current–voltage characterization showed very good rectifying behavior with <3 V forward voltage drop. Single-peak EL centered at 394 nm was observed. The authors attributed the EL to radiative recombination on the AlGaIn side of the heterojunction.

In another work that was recently reported, also from China, ZnO nanorods were grown on top of MgZnO ternary and were also subsequently capped with MgZnO.¹⁰⁶ This formed an MgZnO/ZnO nanorod/MgZnO double heterostructure. In research that was done more than a decade ago, it was already demonstrated that the MgZnO/ZnO nanorod heterointerface provides good band alignment and carrier confinement.¹⁰⁷ Here the bottom MgZnO layer served not only as one of the barrier layers but also as the seed layer for ZnO nanorod fabrication. The MgZnO layer was prepared on an epitaxial p-GaN layer at 300°C by RF magnetron sputtering under an atmosphere of argon and oxygen. The sputtering target consisted of a uniform distribution of small ZnO pellets arranged on an Mg disk with a ZnO/Mg area ratio of 3:7. ZnO nanorods were deposited on top of the MgZnO layer by a hydrothermal growth technique that formed an array of vertical nanowires with average diameter of 160 nm. RF magnetron sputtering was used again to form the top MgZnO layer, followed by a thermal annealing step. The structure was finalized by depositing an AZO layer at the top to act as the n-type contact and current spreading layer. A sputtered silver contact completed the device structure. Indium was used as the p-type contact on the p-GaN layer (see Fig. 6).

Diodes made from this structure showed good current–voltage characteristics though somewhat higher internal resistance because of the presence of two barriers in the double heterostructure. The EL, observed with forward drive voltages from 6 to 16 V, showed emission at five distinct wavelengths: 371, 381, 389, 423, and 490 nm. With increasing bias voltage, the emissions at the two shortest wavelengths increased much more rapidly than those at other wavelengths; making the device a strong UV-emitter. This shows that in such structures multiple carrier injection and recombination pathways are active simultaneously with a shift to band edge emission from ZnO dominating at larger applied bias. A remarkable feature of a double heterostructure ZnO nanorod LED seems to be the reduction of defect level emission at longer wavelengths (500- to 600-nm range). Single-heterostructure devices, such as that reported by Zhang et al., in contrast, show concomitant strong defect band emission, which makes the emission from LED appear

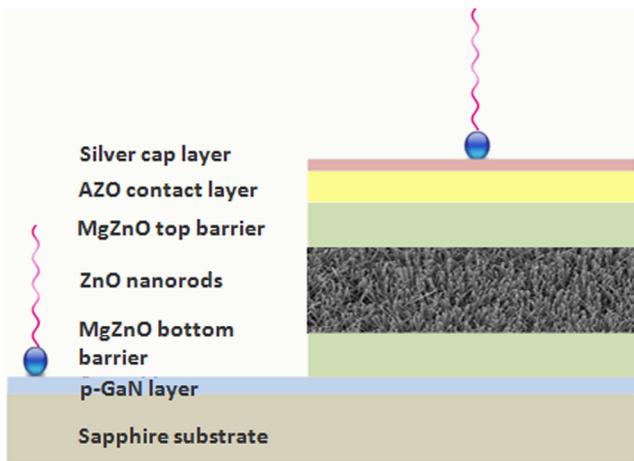


Fig. 6 Device structure of a double heterostructure ZnO nanorod LED.

white.¹⁰⁸ Thus a prominent benefit of a double heterostructure appears to be the reduction of background emission in ZnO nanorods LEDs.

In addition to serving as a heterostructure component, MgZnO can also be coated on ZnO nanowires in order to passivate them from environmental influence. Through aging studies, supported by x-ray photoelectron spectroscopy (XPS), it has been shown that such a coating is beneficial toward the longevity of ZnO nanowire LEDs.¹⁰⁹ This comes about because surface-adsorbed O_2 and OH^- species on bare ZnO nanowires act as acceptor and donor surface states and effectively quench UV EL. Producing a ZnO/MgZnO core/shell structure avoids such deleterious adsorption, thus maintaining UV emission and increasing the longevity of ZnO nanowire LEDs. Surface passivation of reduced dimensionality structures, such as nanowires and quantum dots, is essential for prolonging the operating lifetime of devices that employ these structures. This is, thus, a complication that has to be addressed in order to get the benefits that reduced dimension semiconductor structures confer on functional devices. While this may appear to take some attention away from the main structure of the LED, which is responsible for light emission, its importance should never be underestimated. This is because surface recombination and associated effects can both reduce radiative recombination efficiency and lead to irreversible deterioration (aging) of the device.

In a very recent work reported by a US-China team, Gao et al.¹¹⁰ have described the fabrication and operation of ZnO nanowire Schottky LEDs. They made their devices by depositing gold at the top ends of ZnO nanowire arrays. These devices exhibited clear rectifying characteristics and, at high forward bias currents, excitonic luminescence centered at 380 nm. The UV radiation intensity increased with further increase in drive current. This characteristic clearly showed an excitonic UV LED operation and demonstrated that ZnO Schottky devices are a strong contender for making UV LEDs. It should be noted that a simpler planar metal-insulator-semiconductor ZnO diode employing HfO_2 insulator was already reported back in 2009 by the Chinese team of Huang et al.¹¹¹ Their device emitted 370-nm radiation at a voltage as low as 2 V.

While n-type ZnO nanowires can be paired with planar or nanowire p-type GaN for making heterostructure LEDs, another promising route employs p-type conducting organic polymers for this purpose. This approach is feasible because most conducting polymers show p-type conductivity and can be easily deposited through dip- or spin-coating techniques.¹¹² Furthermore, a large body of work exists on organic LEDs (OLEDs) from which appropriate polymer materials can be chosen for fabricating hybrid organic-inorganic ZnO-based LEDs. Many organic conductors, semiconductors, and light-emitting materials are commercially available from companies such as Merck and American Dye Source. One of the early reports on making hybrid organic-inorganic LEDs using ZnO was the work reported by Könenkamp et al.^{113,114} from Portland State University. An interesting feature of their work is that they deposited ZnO nanowires on an electrically conducting, fluorine-doped, SnO_2 -coated glass substrate using an aqueous solution electrodeposition process.¹¹⁵ n-type doping of the nanowires was performed *in situ* by adding $AlCl_3$ to the solution.¹¹⁶ This type of process is especially suitable for depositing uniform nanowire layers on large area substrates. After growth, the nanowires were encapsulated in polystyrene and topped by a layer of conductive poly(3,4-ethylene-dioxythiophene)-poly(styrene-sulfonate) (PEDOT/PSS) polymer film. A gold contact was deposited at the top of the structure to serve as the anode of the heterostructure LED. On powering up their device, the investigators observed white EL at a current density of 5 mA/cm² (corresponding to 100 mA/cm² at the nanowire tips). The EL spectrum consisted of a broad defect-related luminescence band centered at 620 nm and a weak excitonic peak from recombination in ZnO nanowires at 360 nm. This work clearly showed the need for further progress, both in improving the electrical characteristics of the device and in strengthening the excitonic emission. Workers from the same laboratory later extended their research by depositing ZnO nanowires on flexible ITO-coated polymer substrates.¹¹⁷ This led to a highly flexible ZnO nanowire LED that emitted broadband light under forward bias. It should be noted here that by combining ZnO nanowires with organic electronic materials, flexible light-emitting devices can be constructed. Such devices can find many applications in fields ranging from on-person devices to health care and environmental monitoring.

Yet another example of organic polymer/ZnO nanowire LED was described by an international research collaboration in 2006.¹¹⁸ This group utilized a layer structure consisting of n-type ZnO nanowires grown on an n-type rather than p-type GaN substrate. They filled their nanowire layer with the hole-conducting PEDOT/PSS polymer. A top ITO contact was deposited as the anode while the n-type GaN substrate was used as the cathode of the diode. Electrical characterization revealed that the device had a soft $I-V$ curve. The EL spectrum exhibited several peaks throughout the visible region, the near-IR, and the near-UV. The near-UV peak originated from band-edge recombination in ZnO nanowires, whereas the other peaks came from defect states in the nanowires and at the GaN-ZnO nanowire interface. Co-occurrence of band-edge EL with broad defect band luminescence is a feature that is often observed in heterostructure ZnO LEDs.¹¹⁹ Sometimes, it leads to the light

emission actually appearing white because of the mixing of blue emission from GaN or ZnO with the broad yellow emission from defect states.⁹⁵ The defect state emission then acts as the conventional yellow phosphor used in making white LEDs. This phenomenon has also been observed in GaN-only systems.¹²⁰ At this point, it is worthwhile to mention a very recently reported work where ZnO was specifically engineered to act as a yellow phosphor. Liu et al.¹²¹ have reported the synthesis of ZnO nanoparticles that show bright yellow fluorescence under UV illumination. Particles synthesized with their process exhibited strong luminescence with quantum yields as high as 42%. LEDs made using these ZnO nanoparticles emitted bright yellow light with efficiencies reaching 64.2 lm/W. More recently, there has been significant progress in making LEDs out of ZnO nanoparticles and quantum dots. That work is described later in Sec. 7.

By 2008, further progress had been made in organic–inorganic heterostructure ZnO LEDs and a device emitting somewhat higher optical power at shorter wavelength was demonstrated in China.¹²² The prominent feature of this device was the use of an organic hole injection layer. Such materials are common in OLEDs but had not been commonly used with inorganic materials. Another distinct feature of this work was the deposition of a planar ZnO film on an ITO-coated glass substrate, which was then used for growing ZnO nanowires. After nanowire growth, polymethyl methacrylate (PMMA) was used as an in-fill between individual ZnO nanowires. This produced a planar top surface, which was etched back in oxygen plasma to expose the tops of ZnO nanowires. The hole transport material, *N,N*'-di(naphth-2-yl)-*N,N*' diphenylbenzidine, was then deposited, followed by thermally evaporated high work function silver contact, as the anode of the device. Soft *I* – *V* characteristics were observed with this device. Under forward bias, the light emitted by the diode showed a clear though broad excitonic peak centered at 342 nm, together with a low broad peak at 570 nm. The latter most probably originated from defect states.

In a somewhat similar work, Na et al.¹²³ from the University of Tokyo demonstrated a ZnO/organic heterostructure diode on a silicon substrate. They formed their ZnO film by sputtering and then overlaid it with a layer of p-type organic semiconductor: *N,N*'-diphenyl-*N,N*'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (α -NPD). The junction of these two materials provides comparable energy band offsets between conduction band-lowest unoccupied molecular orbital (1.9 eV) and valence band-highest occupied molecular orbital (2 eV), which makes this system suitable for efficient across-the-interface charge transfer. The authors noted that in order to get very smooth ZnO films through sputtering, which necessarily produces a polycrystalline film, the sputtering process has to be carried out at room temperature with low RF power and no postdeposition annealing. Deposition on a heated substrate and/or annealing the deposited film invariably produces larger grains and thus rougher surfaces that lead to high-interface trap density when the organic layer is subsequently deposited on the sputtered film. For vertical charge transport devices, such as LEDs, polycrystallinity is much less of a problem than is surface roughness. However, mild postdeposition annealing at 150°C was found to be beneficial in relaxing the stress in the as-deposited ZnO film. The EL in their LEDs originated

from defects in ZnO (broadband yellow luminescence) and from the organic layer (narrowband blue luminescence) with no contribution from the band edge of ZnO at all. While the authors argued that this is useful for making LEDs where a specific color can be obtained by varying the relative intensities of the two bands, it is clear that sputtered planar ZnO films do not produce satisfactory LEDs.

A good description of hybrid ZnO LEDs combining ZnO nanowires with organic conductors has been presented by Voss and Waldwogel¹²⁴ from a German University collaboration. In their paper, they have discussed a variety of architectures for such hybrid LEDs and have also suggested a new gas-phase technique for depositing conductive polymers on nanowire arrays.

5.6 ZnO Nanoparticle Heterostructure LEDs

Going beyond nanowires, inorganic/organic ZnO LEDs have also been made from ZnO nanoparticles. In the work reported from the National Taiwan University in 2006, researchers combined vapor phase-grown 90-nm diameter ZnO nanoparticles with *N,N*'-diphenyl-*N,N*'-bis(3-methylphenyl)-1,1'-biphenyl-4, 4'-diamine: poly(methyl methacrylate) to fabricate a hybrid ZnO LED.¹²⁵ The organic component (blended with PMMA) is a hole transport material. An interesting property of this mixture is that on spin coating it segregates into a ZnO nanoparticle layer and a hole transporter layer. The device was made by spin coating the ZnO + hole transporter mixture (in chloroform + toluene) on ITO-coated glass substrate. After a baking step to remove any residual solvent molecules, a 200-nm thick aluminum film was thermally evaporated on top to serve as the LED cathode and back reflector. Good rectification behavior with 4 V forward voltage drop was observed with this diode. On increasing the forward voltage to around 7 V, distinct EL centered at 392 nm was seen. Interestingly, no defect-related broad band emission in the yellow-green region was observed.

5.7 Other ZnO Heterostructure LEDs

While substrates such as sapphire, SiC, or epitaxial GaN are somewhat obvious choices for fabricating heterostructure ZnO LEDs, the use of more unconventional substrates has also been reported. In the work reported from Japan during 2001/2002, an unusual material combination for heterostructure ZnO LEDs was described.^{126,127} Workers there used pulsed laser deposition to deposit epitaxial material layers on yttria-stabilized ZrO₂ single-crystalline substrates. This transparent and refractory material presents an extremely flat surface, which is particularly suitable for epitaxial growth of optoelectronic device structures.¹²⁸ A layer of Sn-doped indium oxide was first deposited to serve as a transparent cathode. This was followed by a ZnO layer and finally a layer of p-type strontium copper oxide (SrCu₂O₂, SCO)—a p-type transparent conducting oxide. Nickel electrodes were deposited at the top of the structure to serve as anode contacts (see Fig. 7). It should be noted that this work was preceded by one from the Tokyo Institute of Technology and TDK Corporation, in which a very similar structure was grown on a glass substrate.¹²⁹ The pn-junction was thus formed between SCO and ZnO. Carrier concentrations in these material layers were of the order of 10¹⁷ cm⁻³. The diode showed very good current–voltage characteristic

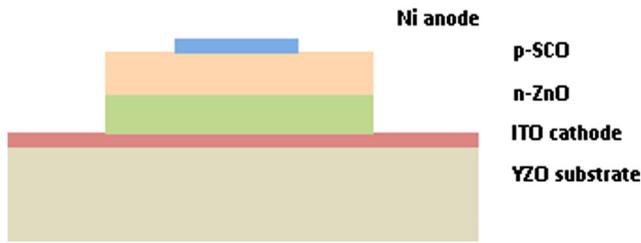


Fig. 7 Layer structure of an n-ZnO/p-SCO heterojunction LED.

with a forward voltage of ~ 3 V and light emission was seen at currents above 10 mA. The peak of emission was found to be at 382 nm, confirming its origin in the ZnO layer of the structure.

It is notable that heterostructure ZnO pn-junction diodes can also be used as short-wavelength photodetectors, in much the same way as GaN-based pn-junction diodes are used as solar-blind photodiodes. An example is provided by the work described by Ohta et al.,¹³⁰ where they fabricated transparent pn-heterojunction diodes from p-type NiO and n-type ZnO. Their photodiodes showed reasonably good behavior at a reverse bias of -6 V where they observed a responsivity of 0.3 A/W—comparable to that of commercial devices.

6 Homojunction ZnO LEDs

ZnO LEDs where both n-type and p-type regions of the pn-junction are made from ZnO are preferred devices because this simple configuration avoids contamination of EL from interface states and from energy levels in the non-ZnO component. Electrical charge transport is also much more straightforward in this case, leading to lower device resistance, cleaner turn on, less heat dissipation, and longer device lifetime.¹³¹ Such devices (see Fig. 8) can produce strong ZnO band edge emission but their lifetime and overall reliability remain of concern.

As mentioned earlier, due to the difficulty of making good p-type material, ZnO LEDs were initially fabricated with various heterojunction structures. The most popular of these have been various combinations of ZnO family semiconductors with III-nitrides. Although satisfactory p-type ZnO is still not available, increasing attention is now being paid toward studying homojunction ZnO LEDs. MBE,



Fig. 8 Broad violet-near-UV light emission from a ZnO-based pn homojunction.

MOCVD, ALD, pulsed laser deposition, and sputtering have all been used to fabricate layer structures needed for homojunction ZnO LEDs. The homojunction devices demonstrated so far are valuable for studying the physics and technology of ZnO LEDs but are far from being a commercial reality. This is because of their low optical power output, high device resistance, high-power dissipation (and thus low efficacy), and short lifetime. In fact, homojunction LEDs can often show poorer performance compared to heterojunction devices if the p-type material is not of sufficiently high quality. For instance, in some cases, pn-homojunction ZnO LEDs have shown blue or violet EL but no luminescence characteristic of true ZnO band edge emission in the near-UV.¹³² It is widely accepted that satisfactory and practical ZnO LEDs will only become possible once the problem of p-type doping of ZnO is finally solved. In what follows, we take a look at some homojunction ZnO LEDs that have been reported in the recent literature with a view toward understanding the improvement this brings about over heterojunction devices explored earlier in this paper.

6.1 ZnO Planar Homojunction LEDs

Pan et al.¹³³ were one of the first to report UV emission from homojunction ZnO epilayer LEDs made through MOCVD on ZnO and sapphire substrates. Much work has been done since on homojunction ZnO LEDs. There are a number of possible ways for creating oppositely doped ZnO homojunction structures. MBE, MOCVD, hydrothermal growth, sputtering, and pulsed laser deposition can all be used to layer materials on top of one another. As an example, Lim et al.¹³⁴ from Gwangju Institute of Technology, South Korea used RF magnetron sputtering at high temperature (900°C) to deposit n-type and p-type ZnO sequentially on a sapphire substrate. Their structure was very simple, consisting of only an n-type and a p-type ZnO layer on sapphire. The Ga-doped, $1.5\text{-}\mu\text{m}$ -thick, n-type ZnO layer had carrier concentration of $2.2 \times 10^{18} \text{ cm}^{-3}$ and mobility of $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Gallium is a preferred dopant for n-type ZnO because it causes less deformation of the ZnO lattice even at high doping concentrations.¹³⁵ The sputtering target was ZnO containing 1 wt. % of Ga_2O_3 . The $0.4\text{-}\mu\text{m}$ -thick p-type ZnO layer was deposited in a similar manner, using a ZnO target containing 1 wt. % of P_2O_5 . Both layers were grown in the same chamber without breaking the vacuum. A rapid thermal anneal at 800°C for 5 min in a nitrogen atmosphere was carried out to activate the acceptors in p-ZnO layer, which had carrier concentration and mobility of $1.0 \times 10^{19} \text{ cm}^{-3}$ and $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. They also grew a structure with a carrier confinement layer in between the n- and p-ZnO layers. The three-layer carrier confinement structure consisted of a 40-nm-thick n-ZnO layer sandwiched between two $\text{Mg}_{0.1}\text{Zn}_{0.9}\text{O}$ layers, each 40 nm thick. The mixed Mg, Zn oxide was deposited by co-sputtering from MgO and ZnO targets with RF power ratio of 1:4. This structure is shown in Fig. 9. $300 \mu\text{m} \times 300 \mu\text{m}$ LEDs were made from both structures using Ti/Au cathode and NiO/Au anode. The current–voltage characteristic of the diodes was extremely good with a forward voltage drop of 3.2 V. The EL spectrum from the homojunction LED consisted of a near band edge emission at 380 nm and a broad deep-level emission at ~ 640 nm. LEDs made from material incorporating carrier confinement structure showed

acceptor dopant in ZnO was substitutional N at O sites. Good rectification characteristics were also observed for diodes built through this particular homojunction growth method. Under forward bias, at low temperature (11 K), the diodes emitted light with two characteristic spectral peaks: a narrow blue-violet peak at 410 nm and a broad yellow-green peak at 520 nm. As the temperature was increased to 200 K, these peaks shifted to 430 and 540 nm, respectively, with decrease in emission intensity, until at room temperature, the EL disappeared completely. The authors concluded that the yellow-green band originated from bulk and interfacial defects, whereas the blue-violet emission was a result of carrier recombination in the p-ZnO layer. Proper ZnO band edge luminescence in the depletion region was not observed in this case because of the low concentration and mobility of holes in the p-type material. This remains as the principal challenge for making good ZnO homojunction LEDs.

A modified MBE approach using O₂ and N₂ gases for the growth of p-ZnO films was reported by the same Chinese group.¹⁴² Again, nitrogen atoms were the acceptors in the ZnO film but O₂ served both to provide the oxygen component of ZnO and to enhance the formation of nitrogen atoms in the N₂ plasma. Because the materials grown were the same, the LEDs fabricated from them also exhibited very much the same characteristics as those grown using NO.^{140,141}

MOCVD for the growth of ZnO homojunction LED structures, among other groups, has been described by Dong et al.¹⁴³ from Dalian and Jilin Universities in China. They used p-type GaAs wafers as growth substrates. Using diethyl zinc and high-purity O₂ gas as the zinc and oxygen precursors, they grew an 800-nm-thick layer of high-resistivity ZnO on top of p-GaAs. This structure was then annealed in oxygen for 1 h to obtain p-ZnO by arsenic diffusion from the substrate. 200 nm of n-ZnO was then grown on top to complete the homojunction structure. LEDs were formed from this structure after etching and metallization processes. The diodes exhibited near-ideal $I - V$ characteristics with a forward voltage drop of around 4 V. The EL was dominated by defect band luminescence in the yellow-green region. On raising the forward current to 150 mA, a small peak at 380 nm due to ZnO band edge emission was observed. This study is a good reminder that a homojunction ZnO LED can show nearly ideal diode characteristics but still little band edge emission. Excitonic and radiative recombination processes are of paramount importance in ZnO LEDs. Their proper physical modeling for a given device structure is necessary before commencing on the growth of any ZnO LED structure.

Direct *in situ* doping of ZnO during MOCVD growth has been described by Zhao et al.¹⁴⁴ They used antimony for p-type doping of ZnO¹⁴⁵ while no dopant was used to grow the n-ZnO film. Diethyl zinc, high-purity oxygen, and trimethyl antimony were used as zinc, oxygen, and antimony precursors, respectively. First, a 500-nm pure ZnO film was grown directly on a c-plane sapphire substrate and then an antimony-doped 300-nm ZnO film was grown on top of it. The undoped ZnO film showed n-type conductivity with electron concentration of $2 \times 10^{18} \text{ cm}^{-3}$, whereas the antimony-doped film showed p-type conductivity with hole concentration of $1.27 \times 10^{17} \text{ cm}^{-3}$. The optimized growth temperatures for the n- and p-type layers were 450°C and

550°C, respectively. LEDs were fabricated by depositing bilayer metals on the n- and p-type films. The underlying n-type film was reached by etching the p-type ZnO film with ammonium hydroxide solution. The diodes showed very good current–voltage characteristics with forward voltage drop of 3.3 V. An interesting observation made by these workers was that whereas the undoped n-type ZnO film showed the usual defect band luminescence in the yellow-green region, no such luminescence was seen from the antimony-doped p-type ZnO. This phenomenon has not been investigated in detail but presumably points to some kind of defect compensation through antimony doping.¹⁴⁶ EL from these diodes exhibited mainly blue light with a small amount of near-UV emission.

Just like in the case of GaN LEDs, silicon substrates have also been used for growing ZnO homojunction LED structures. An illustrative example is the work of Ye et al.¹⁴⁷ from State Key Laboratory of Silicon Materials at Zhejiang University in China. They deposited undoped, n-type and p-type ZnO layers, in turn, on a commercial n-type (100) silicon substrate. First, a 100-nm layer of undoped, pure ZnO buffer layer was deposited by pulsed laser deposition at 450°C in an oxygen ambient. Then 400 nm of Al-doped n-type ZnO was sputtered on top of it by DC magnetron sputtering. This was followed by the deposition of a 450-nm Al-doped ZnO film in the presence of N₂O. This gas supplied nitrogen for p-type doping of the ZnO film. ZnO targets containing 0.15 wt. % Al were used for sputtering. Further details of their growth and doping techniques have been described in other publications.^{148,149} LED devices were fabricated from this material using In/Au (anode) and In/Sn (cathode) metallizations. Just like other homojunction LEDs, in this case too very good $I - V$ characteristics were observed. EL at 110 K showed defect band-dominated luminescence with a small band edge peak, which vanished at higher temperatures.

The team of Mandalapu et al.¹⁵⁰ from the University of California at Riverside also reported a silicon substrate homojunction ZnO LED made from antimony-doped p-type ZnO. Instead of MOCVD, they used MBE for growing their material.¹⁵¹ Their device showed 380-nm EL at temperatures below 200 K, together with significant defect band-related emission. Above 200 K, no band edge emission was seen, but the defect band luminescence was still observed.

Pulsed laser deposition for ZnO homojunction formation has been described by Shukla¹⁵² from the Indian Institute of Technology in Guwahati, India. In this work, p-type, phosphorus-doped ZnO layers and n-type, gallium-doped ZnO layers were deposited on preannealed c-plane sapphire substrates. The depositions were carried out with high-purity ZnO targets containing small admixtures of P₂O₅ and Ga₂O₃ as dopant sources. In between the n- and p-ZnO layers, a five-well MQW region consisting of 5-nm ZnO wells and 8-nm Mg_{0.1}Zn_{0.9}O barriers was deposited. The MgZnO ternary was deposited from targets made from a mixture of MgO and ZnO. An 8-ns pulse-width second harmonic of Nd:YAG laser with a repetition rate of 10 Hz and pulse energy density of 1 to 2 J cm⁻² was used as the ablation driver. The depositions were carried out in a vacuum chamber with a base pressure of 10⁻⁶ Torr. LEDs were formed from this material by standard lithographic patterning followed by wet etching and contact metal deposition.

The LEDs were seen to emit near-UV radiation centered at 392 nm once the forward voltage was increased beyond 7 V. This band edge emission grew in strength as the diode forward voltage was increased further. Very little defect level-related emission in the yellow-green region was observed in this case. The LEDs were, however, short-lived as they degraded in ambient air within a few hours; their light output falling substantially after 8 h from device fabrication. The performance was recovered after annealing the devices in oxygen at 400°C. The author pointed out that this behavior shows the need for the development of good surface passivation techniques for ZnO LEDs. Passivation of ZnO LEDs has not been extensively investigated so far and work clearly needs to be done in this area. In one of very few reports available on this topic in the literature, Wang et al.¹⁵³ have described the passivation of ZnO LEDs with SiO₂ and SiN_x layers for improved device performance.

An interesting technique for forming p-ZnO/n-ZnO homojunction diode structures on silicon substrates has been described in a report from the Ataturk University in Turkey.¹⁵⁴ Workers there used an electrochemical technique to deposit ZnO films containing a variety of dopant elements on a boron-doped p-Si substrate.¹⁵⁵ The dopants included sodium, magnesium, antimony, and titanium; all of which can dope ZnO p-type. ZnO pn-homojunctions were grown by first electrochemically depositing a p-ZnO layer and then an n-type ZnO layer on top. Current-voltage characteristics of all pn-junction diodes showed very good rectifying behavior with low forward voltage drops, in the range of 1 to 2 V. Almost all diodes also showed multipeak EL. A strong blue luminescence was observed together with somewhat weaker defect level-based yellow and red luminescence. The combined luminescence made the emission appear white. It was clear that pn-junctions fabricated with such electrochemical doping and deposition technique exhibit very significant defect-related emission. Thus electrochemical processes, though easy to implement, are generally not suitable for fabricating high-quality LEDs because of their inherently contaminating nature.

Bandgap-engineered ZnO homojunction structures have also been grown through MOCVD. This technique offers the advantage of low-cost growth of large number of wafers in unified batches. In one report from the National Cheng Kung University in Taiwan, the growth of an MgZnO/ZnO/MgZnO quantum well structure has been described.¹⁵⁶ The researchers reporting their work described a specially designed MOCVD system that was used to grow a 25-nm-thick aluminum nitride nucleation layer, a 1- μ m thick undoped GaN buffer layer, and a 600-nm-thick p-type Al_{0.18}Ga_{0.82}N layer, all on a c-plane sapphire substrates. An undoped MgZnO/ZnO/MgZnO quantum well layer was grown on top of p-AlGaIn. The MgZnO barrier layers were each 5-nm-thick, whereas the ZnO well layer was 90-nm-thick. An n-type ZnO layer was grown on top as the cathode contact layer. LED mesas were etched in this material and anode (Ni/Au) and cathode (Ti/Au) contacts were formed on p-AlGaIn and n-ZnO, respectively. Room-temperature PL spectrum of the ZnO films deposited on sapphire substrates and excited by a He-Cd laser with a wavelength of 325 nm showed very sharp and clear emission at 380 nm from ZnO band edge. Almost no sign of defect-related “green” emission at longer wavelengths could be discerned.

LEDs showed very good current-voltage characteristics with forward voltage drop in the 2- to 3-V range. The device resistance was a little high, most probably because of the quantum well structure’s multiple interfaces and the undoped ZnO well layer. Under forward bias, the LED emitted sharp band edge EL with hardly any trace of defect-related emission. A comparison was also made with EL from a p-AlGaIn/ZnO/n-ZnO structure LED, i.e., without the double heterostructure and while similar emission to the quantum well device was observed, its intensity was much weaker. This observation clearly showed that carrier confinement through double heterostructure designs is very effective in raising the internal quantum efficiency of ZnO homojunction LEDs.

At this point, it should be mentioned that yet another system that is promising for LED applications has been very recently realized by Dewan et al.¹⁵⁷ This is the ZnO/NiZnO system prepared by pulsed laser deposition on c-plane sapphire substrate. XPS data showed a type-II band alignment with conduction and valence band discontinuities suitable for making LEDs. Devices have, however, not been fabricated in this system at the time of this writing.

6.2 ZnO Nanowire Homo Junction LEDs

ZnO nanorods have also been used in homojunction structures for making LEDs. These developments have closely followed on similar work performed on GaN nanowires for making high-performance GaN/InGaIn LEDs. In 2008, researchers from Peking University in China demonstrated such a device.¹⁵⁸ The pn-homojunction was formed by growing n-type ZnO nanowires on a p-type ZnO film. High-resistivity silicon was used as the substrate in this work. Spray pyrolysis was first used to form a p-ZnO layer on silicon. An aqueous solution of zinc acetate, ammonium acetate, and indium nitrate was prepared, and the atomic ratio of Zn/N/In in the precursor solution was controlled to be 1:3:0.05. A fine spray was produced using an ultrasonic nebulizer. The spray was transported to the silicon wafer heated to 420°C in a stream of pure oxygen gas. The reactants decomposed at the heated silicon surface to produce a nitrogen-indium co-doped p-type ZnO film. Such a technique for producing p-ZnO films has been known for some time.¹⁵⁹ ZnO nanowires were then grown on the p-ZnO layer using an aqueous co-solution of zinc nitrate and methenamine (hexamethylenetetramine). An ITO-coated glass slide was pushed on top of the ZnO nanowire layer to serve as the cathode of the homojunction diode with the anode being a metallic contact on the planar p-ZnO layer. This device showed a clear rectifying behavior with a forward voltage drop in the region of 4 to 6 V. EL was observed with a sharp 386-nm peak from excitonic band edge emission and a broad 550-nm peak due to defect band emission. The intensities of both emissions were linearly dependent on the forward current through the diode. Room temperature PL experiments clearly showed that the 386-nm emission originated from ZnO nanowires, whereas neither the nanowires nor the p-ZnO film by itself showed 550-nm emission. This was taken as strong evidence for the “green” 550-nm emission originating from defect centers at the junction of the p-ZnO layer and the n-ZnO nanowires.

A more recent report of ZnO nanowire homojunction LEDs has come from Wuhan University in China.¹⁰⁶ In

contrast to the Peking work, researchers at Wuhan University developed a double heterostructure ZnO nanorod LED. In this structure, undoped ZnO nanorods were sandwiched between MgZnO layers. This active homojunction structure was grown on top of a p-GaN-on-sapphire substrate. First, they deposited an MgZnO layer on p-GaN through RF magnetron sputtering at 300°C. The sputtering target consisted of a uniform distribution of small ZnO pellets on an Mg disk with a ZnO/Mg area ratio of 3:7.¹⁶⁰ Subsequently, ZnO nanowires with average diameter of ~160 nm were grown on the MgZnO layer by a hydrothermal process very similar to that described in the previous work. A second MgZnO layer was sputtered on top of the nanowires. Finally, an aluminum-doped ZnO layer was deposited on the top to make an electron-injecting cathode contact. The electrical characteristics of this device showed good diode behavior, whereas the EL exhibited quite sharp band edge emission below 400 nm with only weak emission at longer wavelengths from defect states.

In a very recent publication from a group at Yonsei University in South Korea, Baek et al.¹⁶¹ have described a novel homostructure ZnO—ZnO nanorod array LED, which emitted light under both forward and reverse bias. Interestingly, the emission wavelengths were different depending on biasing polarity. This indicated that the carrier injection and recombination mechanism was bias polarity-dependent. Under forward bias, widely separated emission peaks in the violet, yellow, and red regions were observed at 475, 625, and 700 nm, respectively. On reversing the bias polarity, only a single broad peak centered at 730 nm was seen. The 475-nm emission was attributed to a localized surface plasmon resonance effect that shifted the original 378-nm band edge emission. The research team explained it as arising due to the presence of silver nanoparticles formed after annealing of the Ag top electrode. Due to a different carrier recombination mechanism operating during reverse bias, this emission was not observed while the LED was reverse biased.

ZnO nanowire material growth is a very active research area at this time; much due to the potential of ZnO nanowire-based LEDs. In some very recent work from South Korea, reported by Park et al.,¹⁶² high-quality, individually position-controlled, and vertically aligned ZnO nanotube arrays were grown on CVD-deposited graphene films. The research team, from Seoul National University, demonstrated large-area growth of ZnO nanotubes on a variety of substrates, including amorphous, metallic, and flexible surfaces. Such work will undoubtedly lead to better ZnO nanowire LEDs in the near future as the team has already demonstrated laser action in this material.¹⁶³

7 ZnO Quantum Dot LEDs

In recent years, very small crystallites of ZnO have also emerged as interesting contenders for light generation. Being of the order of 2 to 20 nm in size, these crystallites are small enough to show strong quantum confinement effects and are, thus, also described as ZnO quantum dots. Light-emitting devices can be developed where ZnO quantum dots form the central light-emitting part of the device. In this role, the dots are, generally, embedded in a suitable carrier layer. Making such a device usually starts from synthesizing ZnO quantum dots of a desired size. Sol-gel techniques have been employed for this purpose. Mikrajuddin

et al.¹⁶⁴ have described traditional sol-gel synthesis of ZnO nanocrystallite colloid, which was mixed with a separately produced silica (SiO₂) colloid. On spray drying this mixture, they obtained a nanocomposite powder of mixed ZnO and SiO₂ nanocrystals. PL studies showed that this material exhibited stable green luminescence, which was resistant to aging. The presence of silica, thus, had a beneficial effect on stabilizing ZnO nanocrystals against environmental influences. This observation has been verified by Zhong¹⁶⁵ through a very different process for preparing ZnO quantum dots. Here ion implantation and subsequent thermal annealing were used to create 4- to 10-nm diameter ZnO quantum dots in a silica matrix. Very recently, a Chinese research collaboration has made use of silica-containing ZnO quantum dots to fabricate LED phosphors.¹⁶⁶ They used sol-gel techniques to prepare yellow-emitting silica-encapsulated ZnO quantum dots. The powdered material was then mixed with blue-emitting BaMgAl₁₀O₁₇:Eu²⁺ phosphor. This mixture was used as a phosphor coating on top of a UV-emitting LED. White light generated by this device with luminous efficacy reaching as high as 73.6 lm/W and operating temperature endurance in excess of 110°C. Another similar LED using ZnO quantum dot phosphor has also been described by Chen et al.¹⁶⁷

It should be mentioned here that it is possible to synthesize ZnO quantum dots with various dopant inclusions. Doping of quantum dots is used to modify their physical properties. ZnO quantum dots doped with gadolinium, e.g., have been prepared as combined fluorescent and magnetic probes for magnetic resonance imaging.¹⁶⁸ Doping has also been performed with various alkali metal atoms in order to change the color of fluorescent emission.¹⁶⁹ Furthermore, it has been shown that mixing carbon nanodots with ZnO quantum dots can produce a fluorescent material with enhanced luminous efficiency. A Chinese collaboration has demonstrated a significant improvement of near-UV EL from ZnO quantum dot LEDs *via* coupling with carbon nanodot surface plasmons.¹⁷⁰

Various groups have recently fabricated LEDs that make use of ZnO quantum dots as an emission layer, an electron transport layer or both. Cao et al.¹⁷¹ have reported on the fabrication of highly efficient CdSe/ZnS quantum dot LEDs incorporating a gadolinium-doped ZnO quantum dot electron transport layer. Magnesium-doped ZnO quantum dots have also been used as the electron transport layer in a layered LED made completely out of functional quantum dot layers.¹⁷² Very recently, a CdSe/CdS/ZnS quantum dot LED has also been reported with a sol-gel-synthesized ZnO film as a highly conductive electron transport layer.¹⁷³

The use of ZnO quantum dots for making LEDs is an interesting development. This material can be synthesized by both chemical (sol-gel) and physical (ion implantation) routes. Its PL exhibits two characteristic peaks: a short-wavelength near-UV peak due to bandgap transitions and a long wavelength green peak due to various structural defects in the dots. The first one is tuneable through changes in the size of the quantum dots and thus can be used to obtain UV emission at a desired wavelength in the 360- to 400-nm region. The defect-generated green peak, on the other hand, can be used as a source of green light emission, as has been demonstrated by several groups mentioned

above. The ease with which ZnO quantum dots can be synthesized and the tuneability of their fluorescence are the two principal reasons for the strong interest in this material phase of ZnO. However, the longevity of ZnO quantum dots is the factor limiting their widespread use at this time. Once proper encapsulation techniques have been developed to prolong their usable lifetime, this material will likely emerge as a serious contender for making both UV and green-emitting LEDs. Another reason for the popularity of ZnO quantum dots is due to the fact that they can be used both as an intrinsic light-emitting layer when integrated inside the structure of LEDs and as an external phosphor when coated on top of blue or UV LEDs.

8 End Note

Where do we stand on ZnO LEDs today? This survey makes it clear that much needs to be done to improve the operating characteristics of these devices in order to get closer to their commercialization. Interestingly, it appears that good heterojunction ZnO LEDs can be better than the not-so-good homojunction LEDs that bring the focus to the development of high-quality ZnO pn-junctions. It is indisputable that for commercial ZnO LEDs to make appearance we need much more progress toward the development of p-type ZnO with respectable and enduring hole-mediated conduction. Thus the situation with ZnO currently is the same as was the case with GaN many years ago before workable methods for p-type doping of GaN were developed. Only with the availability of proper p-ZnO high-quality homojunction ZnO LEDs will be realized. Such LEDs will emit only bandgap light with very little, if any, defect level emission. Commercial LEDs will need to be efficient, reliable, and long-lived with reasonable manufacturing costs. Electrically, these devices will have to have low forward drop voltage (compatible with the bandgap of ZnO and thus in the range of 3 to 3.5 V) and low overall device resistance. Experimental homojunction ZnO LEDs that have been demonstrated so far fall short of these goals. However, it is very heartening to note that throughout this century so far, progress, although slow, is continually being made in this field.^{174–176} Once commercial ZnO LEDs make their appearance, further progress will be very rapid because much that has been learned over the years with the development of GaN LEDs can be applied to ZnO LEDs as well. Thus such evolved variants as photonic crystal LEDs, resonant cavity LEDs, and nanowire LEDs could also be commercial realities soon after plain homojunction ZnO LEDs are commercialized. It is not inconceivable that in the coming years there may be a breakthrough in p-doping of ZnO and a new device emitting blue and UV light then makes its appearance.^{177,178}

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