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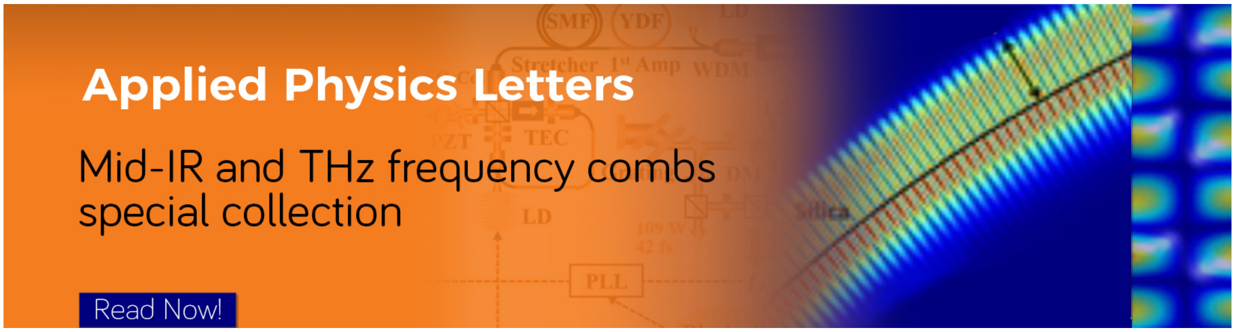

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Phosphorus doped ZnO light emitting diodes fabricated via pulsed laser deposition

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ZnO-based light emitting diodes were fabricated on *c*-plane sapphire using ZnO:P/$Zn_{0.9}Mg_{0.1}O$/ZnO/$Zn_{0.9}Mg_{0.1}O$/ZnO:Ga *p-i-n* heterostructures. The *p-i-n* heterojunction diodes are rectifying and show light emission under forward bias. The electroluminescence spectra shows deep level emission at low bias, but near band edge ultraviolet emission at high voltage bias. A decrease in leakage currents in as-fabricated structures was achieved via low temperature oxygen annealing. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2900711]

ZnO is an interesting optoelectronic material due to its large direct bandgap and high exciton binding energy.[1–5] Incorporating ZnMgO or ZnCdO layers make it possible to fabricate bandgap modulated quantum well structures.[6,7] Significant efforts have been directed toward the fabrication of ZnO thin film[8,9] and nanowire[10,11] devices, including rectifying[12–15] and light emitting diodes (LED). Lim *et al.* have reported the fabrication of ZnO based LEDs using sputter deposited P-doped ZnO as the *p*-type layer.[16] Ryu *et al.* employed BeZnO/ZnO quantum wells and obtained UV electroluminescence (EL).[17] Tsukazaki *et al.* fabricated a *p*-ZnO/*i*-ZnO/*n*-ZnO LED on $ScAlMgO_4$ by using repeated-temperature-modulation epitaxy for the *p*-type ZnO:N layer.[18] Liu *et al.* reported EL from a ZnO homojunction LED grown on a single crystal ZnO.[19] Ye *et al.* used N–Al codoping for *p*-type doping and fabricated ZnO LEDs on Si with sputter deposition.[20] In all cases, the reported light emission intensity from the ZnO LEDs was relatively weak. A significant challenge in developing ZnO LEDs is the formation of *p*-type material.[21] Despite this challenge, many groups have reported on successful *p*-type doping with several dopants.[22–24] In recent studies, we have investigated the growth of *p*-type ZnO in P-doped ZnO grown by pulsed laser deposition (PLD).[25–29] In this paper, the synthesis and properties of ZnO LED heterojunctions employing these P-doped ZnO materials is reported.

The ZnO thin film structures were fabricated on sapphire (0001) substrate using PLD.[30] P and Ga were used as the *p*- and *n*-type dopants, respectively. Prior to LED epitaxial film deposition, an undoped ZnO buffer layer was deposited on the sapphire at 400 °C and a pressure of 20 mTorr as a nucleation layer, then annealed at 650 °C. The subsequent epitaxial films were grown in an O_2 pressure of 150 mTorr. The LED structures consist of 250 nm of P-doped ZnO, 40 nm of undoped $Zn_{0.9}Mg_{0.1}O$, 40 nm of ZnO, 40 nm of $Zn_{0.9}Mg_{0.1}O$, and 450 nm of Ga-doped ZnO. Figure 1 shows a schematic of the device structure. The epitaxial films were grown at 700 °C. P-doped ZnO targets were fabricated using high purity (99.9995%) ZnO mixed with P_2O_5 (99.998%) as the doping agent. The P doping level was 0.5 at. %. Ga-doped ZnO targets were fabricated with high purity (99.9995%) ZnO mixed with gallium oxide (99.998%) as the doping agent. The gallium doping level was 1 at. %. The carrier concentration in the P and Ga doped ZnO layers were estimated to be 1×10^{17} and 5×10^{19} cm^{-3}, respectively, based on Hall measurements performed on single layer films grown under the same conditions. All targets were sintered at 1000 °C for 12 h in air. The targets were ablated with a KrF excimer laser at a laser frequency of 1 Hz and energy density of approximately 1.5 J/cm^2.

Prior to the LED fabrication, the ZnO multilayered structures were annealed in a rapid thermal annealing (RTA) system at 900 °C for 1 min under an oxygen ambient to activate the *p*-type dopant. The LED fabrication started with device isolation and followed with *p*-mesa definition using dilute phosphoric acid solution. Electron beam deposited Ni (20 nm)/Au (80 nm) and Ti (20 nm)/Au(80 nm) were used as the *p*- and *n*-Ohmic metallization.[31,32] The current-voltage characteristics were measured using an Agilent 4145B parameter analyzer. The EL spectra were measured with a Princeton Instrument spectrophotometer equipped with a charge-coupled device array. The total light output power was measured by a Si photodiode. Also, photoluminescence (PL) measuments were performed with a He–Cd laser.

The *I-V* characteristics of the as-fabricated diodes showed high leakage currents. There was limited diode rec-

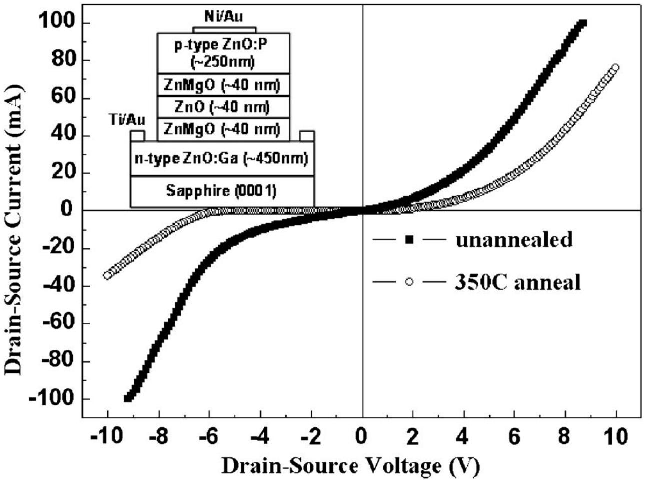

FIG. 1. *I-V* characteristics for a ZnO:P/$Zn_{0.9}Mg_{0.1}O$/ZnO/$Zn_{0.9}Mg_{0.1}O$/ZnO:Ga heterojunction diode both as-fabricated and after 350 °C annealing. Also shown in the inset is a schematic of the device structure.

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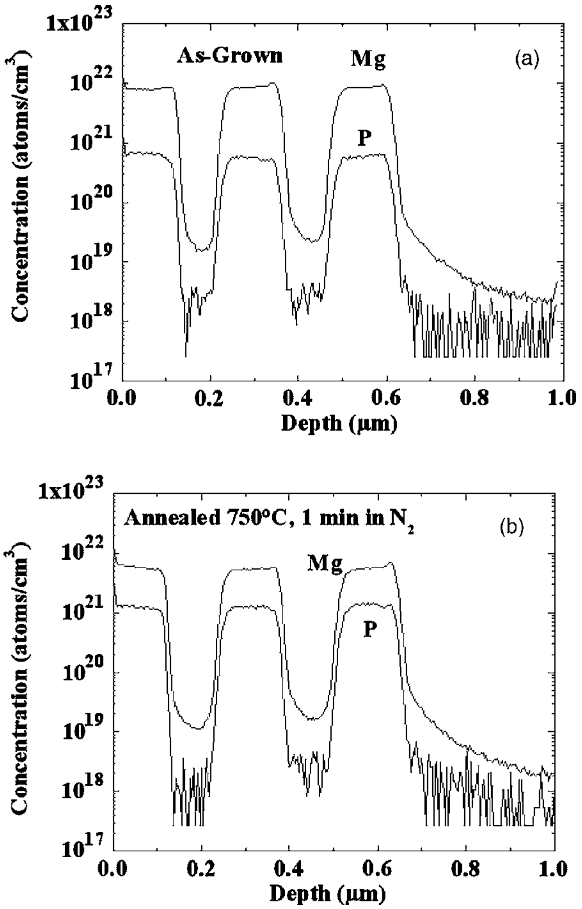

FIG. 2. SIMS composition depth profile taken for a ZnMgO:P/ZnO multilayer both (a) without and (b) with postgrowth annealing.

tification and light emission. However, if the fabricated diodes were annealed at 350 °C for 5 min in O_2, rectifying *I-V* characteristics and EL were observed. These results are shown in Fig. 1. Note that annealing at 350 °C in oxygen should do little or nothing to either the oxygen content or P location within the bulk of the structure given that the films were grown at 700 °C and annealed at 900 °C prior to device wet processing. The stability of the P doping profiles to high temperature growth and annealing can be seen in Fig. 2. Here, the secondary ion mass spectrometry (SIMS) profiles of ZnO/ZnMgO:P multilayers are examined both as-grown and annealed. The profile for the as-grown ZnO/ZnMgO:P multilayer shows no evidence for significant P interdiffusion across ZnO/ZnMgO interfaces during growth despite the fact that growth occurred at 700 °C. Figure 2(b) shows the SIMS profile for a multilayer structure subjected to a 1 min rapid thermal annealing in N_2 at 750 °C. Again, no evidence for P diffusion across the ZnO/ZnMgO heterointerface is observed.

TABLE I. Resistivity for P-doped ZnO thin films before and after wet etching.

Sample		Resistivity (Ω cm)
RTA 900 °C	Before etching	38.605
	After etching	9.3952
RTA 950 °C	Before etching	1.9089
	After etching	0.957

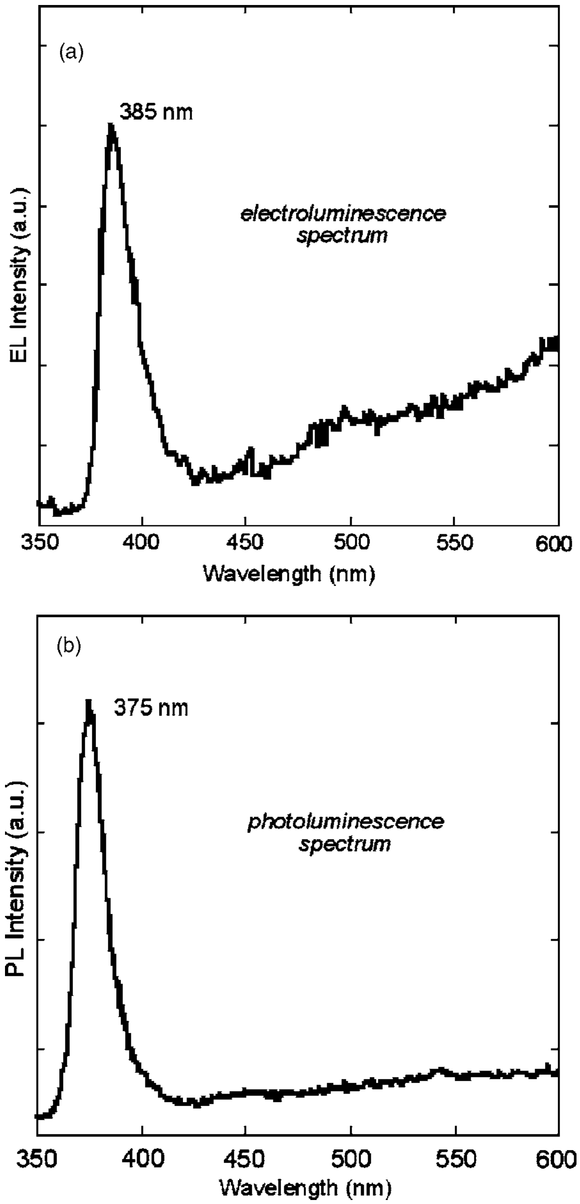

FIG. 3. Room temperature optical spectra of a ZnO:P/$Zn_{0.9}Mg_{0.1}O$/ZnO/$Zn_{0.9}Mg_{0.1}O$/ZnO:Ga heterojunction diode for (a) EL and (b) PL.

While the 350 °C annealing in oxygen has little impact on bulk O or P content, it does appear to eliminate surface and mesa sidewall conduction that was introduced when the LED structure was fabricated by wet etching and photolithography. Table I shows the effect of wet etching on the resistivity. The table shows P-doped ZnO film resistivities measured before and after a moderate wet etching exposure to dilute phosphoric acid. As seen in Table I, the extrapolated resistivity (assuming uniform carrier density distribution) decreases significantly with exposure to the etchant. The carrier type of the etched samples was *n*-type. The origin of this increase in conductivity could be metallization of the surface or incorporation of hydrogen as a donor. Hydrogen can be easily incorporated into ZnO during processing.[33–36] Regardless of the origin, the 350 °C anneal eliminates this conduction path.

The metal contacts were confirmed to be Ohmic by linear *I-V* curves. Turn-on voltage for this device was ~2.2 V, which is lower than what would be anticipated for a *pn* junction for a 3.2 eV semiconductor. Although light emission intensity varied linearly with drive current, the near band edge EL peak does not emerge until the applied voltage is 7 V or greater. Given that the device is a planar structure, the voltage drop will occur partially along the planar current path, partially across the junction. Figure 3 compares the EL and PL spectra for the LED heterostructure. The EL spectra shows the peak at 385 nm. This peak is slightly shifted to the longer wavelengths relative to the PL observed for the same structure. The origin of this shift is unclear. Also, the EL spectrum shows more visible emission intensity than that seen in the PL spectrum.

In conclusion, ZnO LEDs were fabricated utilizing P-doped thin films grown by PLD. The heterojunction diodes using $\mathrm{ZnO:P/Zn_{0.9}Mg_{0.1}O/ZnO/Zn_{0.9}Mg_{0.1}O/ZnO:Ga}$ layer showed diode characteristics having ~2.2 eV turn-on voltage. The EL spectra showed the near bandedge emission with some deep level emission.

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