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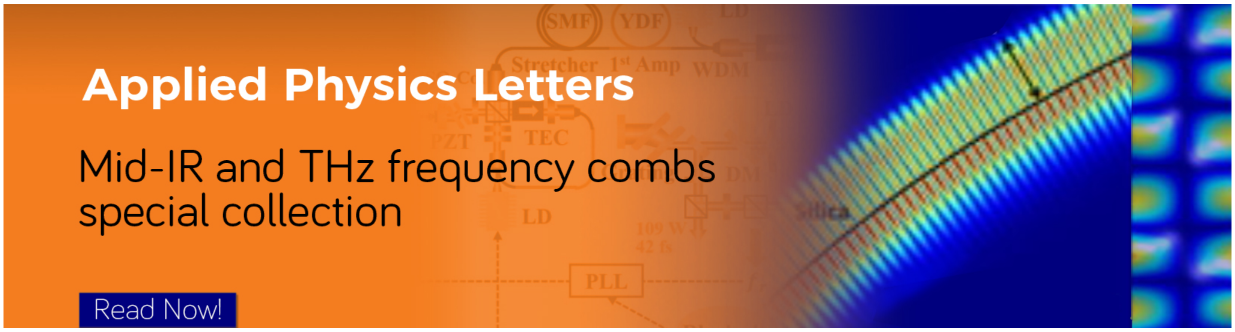

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$Zn_{0.9}Mg_{0.1}O/ZnO$ *p–n* junctions grown by pulsed-laser deposition

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The electrical characteristics of $Zn_{0.9}Mg_{0.1}O/ZnO$ *p–n* junctions grown by pulsed-laser deposition on bulk, single-crystal ZnO substrates are reported. The forward turn-on voltage of the junctions was in the range 3.6–4 V for Pt/Au metallization used for the *p*-Ohmic contact on $Zn_{0.9}Mg_{0.1}O$.The reverse breakdown voltage is as high as 9 V, but displays a small negative temperature coefficient of -0.1–$0.2\ \mathrm{V\,K^{-1}}$ over the range 30–200 °C. The achievement of acceptable rectification in the junctions required growth of an *n*-type ZnO buffer on the ZnO substrate prior to growth of the *p*-type, phosphorus-doped $Zn_{0.9}mg_{0.1}O$.Without this buffer, the junctions showed very high leakage current. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1783015]

ZnO continues to attract interest for its potential applications in transparent electronics, (UV) light emitters, chemical sensors, spintronics, and varistors.[1–12] Bulk single-crystal ZnO substrates are commercially available and thin films are readily grown by conventional epitaxial techniques as well as pulsed laser deposition and ZnO can be deposited in polycrystalline form at low temperatures onto cheap, transparent substrates such as glass. ZnO nano-rods are also attracting interest for sensor and data storage applications.[12,13] Recent reports of *p*-type doping,[8,9,14,15] aided by theoretical work,[7,16,17] are indicative that minority carrier devices such as light-emitting diodes, laser diodes, and transparent *p–n* junctions are likely to be achieved in the future. Alivov *et al.*[18,19] have recently made progress in that direction by demonstrating electroluminescence from *p*−AlGaN/*n*-ZnO junctions.

We have found that an effective and reproducible route to achieving *p*-type material in the ZnO system is to lower the *n*-type background by adding mg to increase the bandgap and then to dope the ZnMgO with *P* at high concentrations, followed by annealing to obtain type conversion to *p*-type.[10,11,14] The resulting material has been demonstrated to be *p*-type from the capacitance–voltage properties of metal/insulator/*P*-doped (Zn,Mg)O diode structures which exhibit a polarity consistent with the P-doped (Zn,Mg)O layer being *p*-type.[20] In addition, thin-film junctions comprising *n*-type ZnO and *P*-doped (Zn,Mg)O display asymmetric current–voltage (*I–V*) characteristics that are consistent with the formation of a *p–n* junction at the interface. Simple Schottky contacts formed on the ZnMgO also show *I–V* characteristics that are consistent with the material being *p*-type.

In this letter, we report on the temperature dependence of *I–V* characteristics of $Zn_{0.9}Mg_{0.1}O/ZnO$ *p–n* junctions grown by pulsed laser deposition on bulk, single-crystal ZnO substrates. The *p–n* junctions exhibit negative temperature coefficients for reverse breakdown voltage.

The starting substrates were (0001) undoped grade I quality bulk, single-crystal ZnO crystals from Cermet. The samples were epiready, one-side-Zn-face-polished by the manufacturer. The room temperature electron concentration and mobility established by van der Pauw measurements were $10^{17}\ \mathrm{cm^{-3}}$ and $190\ \mathrm{cm^2/V\,s}$, respectively. Pulsed-laser deposition was used for film growth. Phosphorus-doped $(Zn_{0.9}Mg_{0.1})O$ targets were fabricated using high-purity ZnO (99.9995%) and MgO (99.998%), with P_2O_5 (99.998%) serving as the doping agent. Use of the (Zn,Mg)O alloy reduces the residual *n*-type conductivity due to shallow defect donor states. The addition of Mg moves the conduction band edge up in energy and potentially away from the intrinsic shallow donor state, thus increasing the activation energy of the defect donors. The ablation targets were fabricated with a phosphorus doping level of 2 at.%. A KrF excimer laser was used as the ablation source. A laser repetition rate of 1 Hz was used, with a target to substrate distance of 4 cm and a laser pulse energy density of 1–3 J/cm^2. The ZnO growth chamber exhibits a base pressure of 10^{-6} Torr. Film growth was performed at 400 °C in an oxygen pressure of 20 mTorr. Previous work has shown that as-deposited phosphorus-doped ZnO films are heavily *n*-type due to a compensating donor defect.[20] A moderate temperature anneal suppresses the *n*-type behavior considerably. The samples were annealed *in situ* at 600 °C in a 100 Torr O_2 ambient for 60 min. We found it necessary to grow a 0.8-μm-thick buffer of undoped (*n*-type) ZnO prior to growing the ZnMgO in order to achieve acceptable *p–n* junction quality. Without

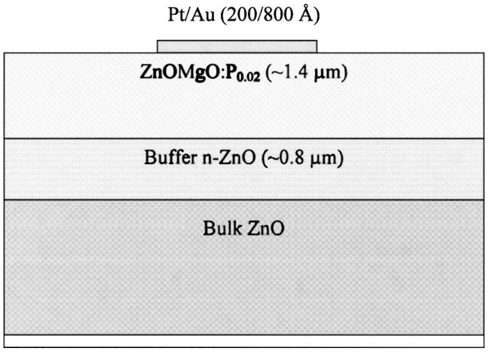

FIG. 1. Schematic of ZnMgO/ZnO *p–n* junction structure.

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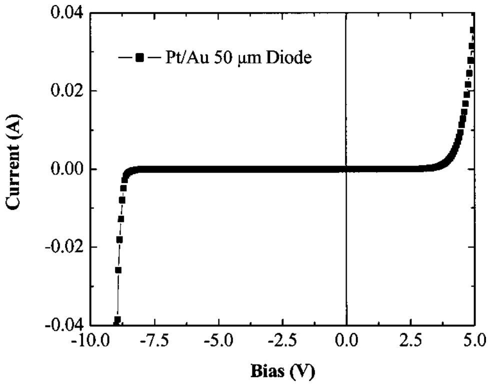

FIG. 2. $I-V$ characteristics at 30 °C of ZnMgO/ZnO $p-n$ junctions using Pt/Au as the Ohmic contact to p-type ZnMgO.

this buffer, the junctions displayed very poor rectification. The buffer was followed by 1.4 μm of ZnMgO:$P_{0.02}$. The p-sides of the structures were contacted with Pt/Au(200/800 Å) deposited by e-beam evaporation and patterned by lift-off with contact diameters ranging from 50 to 375 μm. The bulk ZnO substrate was given a Ti/Al/Pt/Au(200/400/200/800 Å) full-back-side contact annealed at 200 °C for 1 min in N_2. A schematic of the final structure is shown in Fig. 1. The $I-V$ characteristics were measured at temperatures up to 200 °C on a heated probe station using an Agilent 4145B parameter analyzer.

$I-V$ characteristics at 30 °C from the $p-n$ junction structures are shown in Fig. 2. The devices show clear rectification and polarity consistent with the ZnMgO being p-type. We confirmed the linearity of the $I-V$ characteristics between adjoining Pt/Au contacts on top of the p-type ZnMgO, i.e., measuring the structures in a lateral direction produced Ohmic behavior while the vertical structure showed rectifying characteristics. This confirms the presence of a $p-n$ junction. Table I shows the extracted values of reverse breakdown voltage (V_{RB}), saturation current density (J_S), forward voltage drop (V_F), and on-state resistance (R_N).The forward voltage drop of $p-n$ junction rectifiers can be written as

$$V_F=\frac{kT}{e}\ln\left(\frac{n_-n_+}{n_i^2}\right)+V_m,$$

where k is Boltzmann's constant, T the absolute temperature, e the electronic charge, n_- and n_+ the electron concentrations in the two end regions of the $p-n$ junction (the p^+-n and n^+-n regions), and V_m is the voltage drop across the buffer region. Thus it is important to have a high quality buffer in order to minimize the turn-on voltage. At low current densities (<1 A cm^{-2}), the heterojunctions showed thermally activated behavior,

$$J\ \alpha\ \exp\left(\frac{-E_a}{KT}\right)\cdot\exp\left(\frac{e(Vbi-V)}{nkT}\right),$$

where E_a is the activation energy, n the ideality factor, V_{bi} the junction built-in bias, and V is the total applied voltage.[21] The band-offsets in this heterojunction system are much larger in the conduction band (~0.19 eV for ZnO/$Zn_{0.9}Mg_{0.1}O$),[22] compared to the valence band (~20 meV).[22] The rectifiers showed $Ea\sim 1.7$ eV but unphysically large ideality factors, which is consistent with several transport mechanisms being present, including defect–assisted tunneling and conventional carrier recombination in the space-charge region via a deep level near midgap in the ZnMgO.[23] The activation energy is consistent with the presence of midgap recombination centers.

TABLE I. Characteristics of p-ZnMgO/n-ZnO junctions measured on diodes with diameter 50 μm.

	Pt/Au
V_{RB} (eV)	−9.0
J_s(A cm^{-2})	4.6×10^{-9}
V_f	4.0
R_{on} (mΩ cm^{-2})	14.5

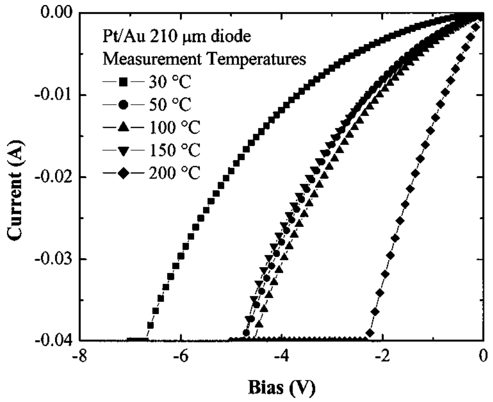

FIG. 3. Reverse $I-V$ characteristics of ZnMgO/ZnO $p-n$ junctions using Pt/Au as the Ohmic contact on the p-type ZnMgO, as a function of the measurement temperature.

Figure 3 shows the temperature dependence of reverse $I-V$ characteristics for the Pt/Au contacted junctions. The reverse breakdown voltage (V_{RB}) decreases with temperature, T. The variation of V_{RB} with temperature is plotted in Fig. 4. The data can be represented by a relation of the form:

$$V_{RB}=V_{RB0}[1+\beta(T-T_0)],$$

where the breakdown voltage showed a slightly negative temperature coefficient, β, of 0.1–0.2 V K^{-1}. It is desirable to have a positive temperature coefficient for breakdown if high temperature applications are envisaged, although both SiC and GaN devices typically showed negative values in the

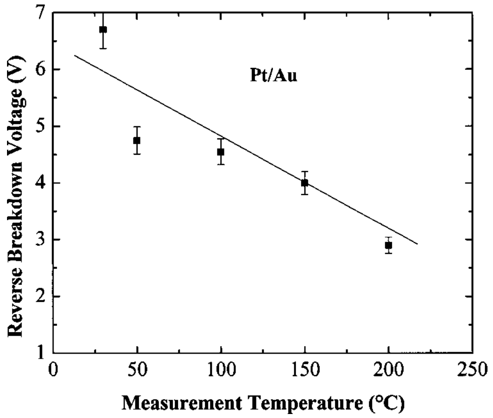

FIG. 4. Measurement temperature dependence of the reverse breakdown voltage in ZnMgO/ZnO $p-n$ junctions using Pt/Au as the Ohmic contact on p-type ZnMgO.

early stages of their development due to the presence of defects and non-optimized growth and processing. There is still room for optimization in both the growth and processing conditions for the $p-n$ junctions.

In summary, we have demonstrated ZnO-based $p-n$ junctions using the ZnMgO/ZnO heterostructure system. The use of an n-type ZnO buffer on the ZnO substrate is critical in achieving acceptable rectification in the junctions. This is an important step in realizing minority carrier devices in the ZnO system.

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