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Citation: Applied Physics Letters **94**, 232101 (2009); doi: 10.1063/1.3149699
View online: http://dx.doi.org/10.1063/1.3149699
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Carrier compensation by deep levels in $Zn_{1-x}Mg_xO$/sapphire

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(Received 13 April 2009; accepted 15 May 2009; published online 8 June 2009)

A systematic analysis of the deep level spectrum in the lower half of the bandgap of Au–$Zn_{1-x}Mg_xO$ ($0.056<x<0.18$) Schottky diodes is presented. Two deep levels are observed at E_v+580 and E_v+280 meV regardless of the bandgap energy with trap concentrations linearly increasing with the Mg content. The E_v+280 meV trap concentration becomes as high as 1.01×10^{18} cm^{-3} at 18% Mg, partially compensating the films and causing a decrease from 8.02×10^{16} to 1.27×10^{16} cm^{-3} in the net electron concentration and an increase by three orders of magnitude in the diode series resistance due to electron trapping. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3149699]

The possibility to extend the bandgap of ZnO to higher energies in the UV can be achieved through alloying with Mg, which if left below 35%–40%, maintains the wurtzite structure of ZnO. As a result of this control over bandgap energy $Zn_{1-x}Mg_xO$ can be used as a barrier for carrier confinement in $Zn_{1-y}Cd_yO/ZnO/Zn_{1-x}Mg_xO$ heterostructures,[1] or as an active layer in UV photodetectors,[2] especially now that Schottky diodes with good rectification properties can be obtained.[3] Interestingly enough, $Zn_{1-x}Mg_xO$ has also been used by several groups to achieve more efficient *p*-type doping than in ZnO,[4–6] and thus to demonstrate *p-n* junctions.[5,7] It has been suggested that this enhancement in *p*-type doping efficiency may be related to a decrease in the efficiency of the residual donors resulting from an upwards shift of the conduction band edge with the Mg content.[5] Other reports postulate an enhancement of the density of V_{Zn} with increasing Mg.[4] We present here a systematic analysis with the Mg content of the formation and concentration of deep levels found throughout the lower half of the bandgap of *a*-plane $Zn_{1-x}Mg_xO$. A combination of deep level optical spectroscopy (DLOS) (Ref. 8) and lighted capacitance-voltage profiling (LCV) (Ref. 9) are used since they allow the quantification of the energies and concentrations of the deep levels found in the lower half of the bandgap of *n*-type material, i.e., deep levels that may act as acceptors.

A-plane unintentionally doped *n*-type $Zn_{1-x}Mg_xO$ films were grown on *r*-plane sapphire by remote plasma enhanced metal-organic chemical vapor deposition. A VI/II flux ratio of 270 (O-rich conditions) was used for all the films, whereas the Mg concentration was varied from 5.6% to 18.0% leading to a bandgap energy shift of ~200 meV. Details of the growth can be found in Ref. 10. Semitransparent Schottky diodes were fabricated by depositing a 100-Å-thick Au layer on the films, whose surface had been previously treated with H_2O_2.[3] The Schottky diodes had areas varying from 3.14×10^{-4} to 1.26×10^{-3} cm^2. Coplanar to the Schottky contacts, extended Ohmic contacts were obtained with a 1000-nm-thick Ti/Al/Ti/Au layer. The Schottky diodes exhibited excellent rectification characteristics (Fig. 1) with Schottky barriers of ~0.95–1.15 eV and forward currents limited by a series resistance (R_s) that increases with the Mg content (Fig. 1). The origin of this effect will de discussed below.

To determine the net carrier concentration in these films, *CV* profiling was performed in the dark. The diodes were allowed to rest in the dark for several hours to minimize the effect of the photogenerated free charge. While the film containing 5.6% Mg had a net electron concentration of 8.02×10^{16} cm^{-3}, increasing the Mg content is followed by a decrease of the electron concentration, which goes down to 1.27×10^{16} cm^{-3} at 18.0% Mg (Table I). Indeed, decreases in the net carrier concentration of $Zn_{1-x}Mg_xO$ with increasing Mg have been reported in the literature.[4,6]

To investigate the origin of this effect, DLOS has been used to probe the deep level spectrum, especially focusing in the lower half of the bandgap. From this analysis both the steady state photocapacitance (SSPC) and the transient capacitance can be extracted as a function of incident photon energy (see Ref. 8 for a review of DLOS). A 1000 W Xe lamp was used as the light source, which was spectrally resolved in a 1/4 m monochromator. The diodes were kept at room temperature under 0 V, with a 30-s-long fill pulse in the dark prior to each light exposure. The resulting SSPC spectra for the four $Zn_{1-x}Mg_xO$ samples are shown in Fig. 2. In these spectra the positive onsets correspond to the optical emission

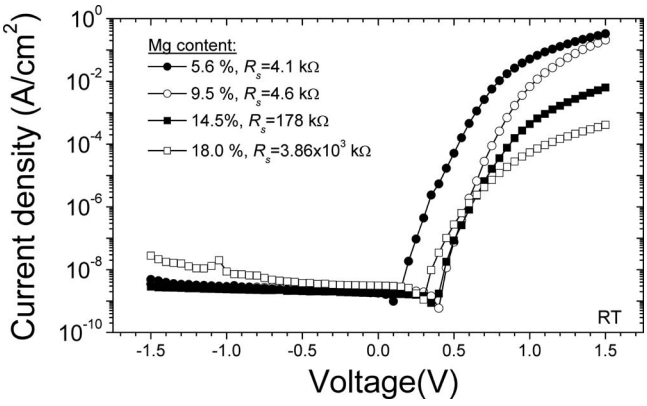

FIG. 1. *IV* curves for the $Zn_{1-x}Mg_xO$ films measured in the dark. The series resistance (R_s) of the Schottky diodes is also shown.

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TABLE I. Trap concentration and net carrier concentration (N_d-N_a) in the $Zn_{1-x}Mg_xO$ films.

Mg content (%)	N_d-N_a (cm^{-3})	E_v+280 meV (cm^{-3})	E_v+580 meV (cm^{-3})	N_t for rest of bandgap (cm^{-3})
5.6	8.02×10^{16}	1.08×10^{17}	1.66×10^{16}	2.59×10^{16}
9.5	1.98×10^{16}	3.44×10^{17}	1.54×10^{16}	2.56×10^{16}
14.5	1.47×10^{16}	8.62×10^{17}	2.27×10^{16}	1.20×10^{16}
18.0	1.27×10^{16}	1.01×10^{18}	5.23×10^{16}	2.54×10^{16}

of electrons from the deep level to the conduction band, whereas the peak found at the highest illumination energy corresponds to the bandgap energy. While the continuous increase of $\Delta C/C_o$ from the lowest illumination energy did not allow the identification of clear onsets in the upper half of the bandgap, two well defined onsets are observed in all samples in the lower half of the bandgap. Subtracting the energy of the onsets from the bandgap energy of each sample, the deep level energy can be referred to the valence band edge. Most interestingly, the same deep level energies are present in all samples, at E_v+580 and E_v+280 meV, which move with the valence band edge as the bandgap energy is increased by adding Mg.

To correctly quantify the optical ionization energy (E^o) of these deep levels, differential capacitance transient analysis close to $t=0$ was performed in the DLOS data, providing the shape of the optical cross section $\sigma^o(h\nu)$ (Fig. 3). A clear sharp onset can be observed in all samples consistent with an effective-masslike state, which describes well shallow levels that are not strongly coupled to the lattice.[11] This onset agrees well with that obtained at E_v+280 meV in the SSPC spectra. Thus, the theoretical Lucovsky's optical cross section[11] has been fitted to the data (Fig. 3), producing values for E^o of E_v+290 (±10) meV, in great agreement with the SSPC onsets. In the case of the deep level observed at E_v +580 meV in the SSPC spectra, its optical cross section could not be well resolved. However, as observed in Fig. 3 for the samples with 5.6% and 9.5% Mg, the onset seems quite broad suggesting there could be strong coupling to the lattice. Thus, it is possible that E^o for this deep level is greater than the value observed in the SSPC spectra, the difference being given by the Franck-Condon shift.[8]

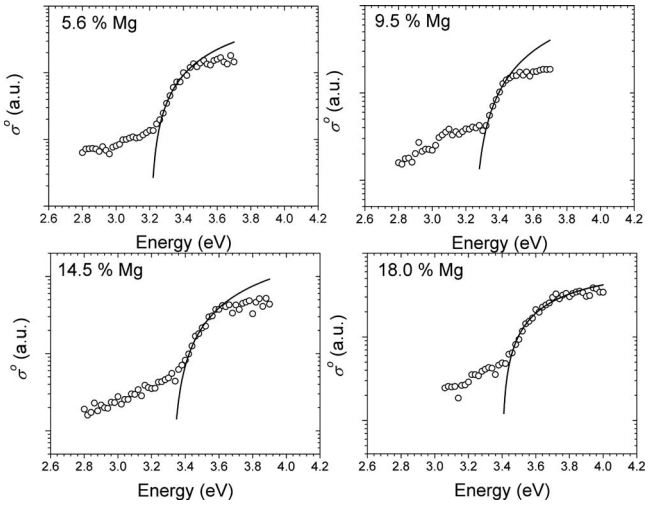

FIG. 3. DLOS spectra from the $Zn_{1-x}Mg_xO$ films. In all cases fits to Lucovsky's model (solid lines) lead to $E^o \sim E_v$+290 (±10) meV.

As shown in Fig. 2, the $\Delta C/C_o$ response from the E_v +580 and E_v+280 meV levels clearly increases as the Mg content increases in the film, indicating an increase in trap concentration (N_t). However, the fact that for all the samples $\Delta C/C_o > 1$ implies that $N_t \sim N_d^+$, and that due to the photoionization of the deep levels there is a significant change of depletion region space charge.[9] This means that when the photodiodes are exposed to incident light of sufficient energy to excite these deep levels, the carrier concentration in these films is fixed by the photoexcited electrons that were initially trapped in the deep levels. Thus, in order to properly quantify N_t, LCV profiling has been used following the approach by Armstrong *et al.*[9] The illumination energy is chosen from the SSPC spectra to control the deep levels that are being photoionized. Note that the deep levels are considered to be filled with electrons prior to the LCV measurement since they are found very deep from the conduction band edge and negligible thermal emission to this band is expected at room temperature.

As an example, the LCV profiles and the resulting electron carrier concentrations are shown in Fig. 4 for the sample with the highest Mg concentration. This diode was measured in the dark and under exposures to 3.10, 3.38, and 3.66 eV light, i.e., using energies slightly below the optical ionization energy of each deep level. In the case of the E_v+280 meV

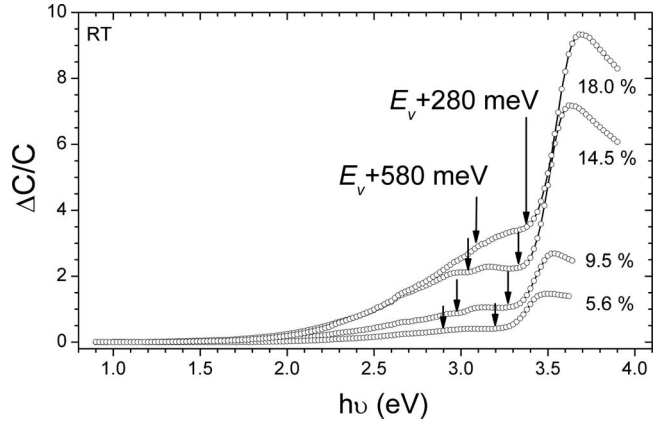

FIG. 2. SSPC spectra obtained in the $Zn_{1-x}Mg_xO$ films where the Mg content is shown next to each curve. All four spectra show two onsets at E_v +280 and E_v+580 meV.

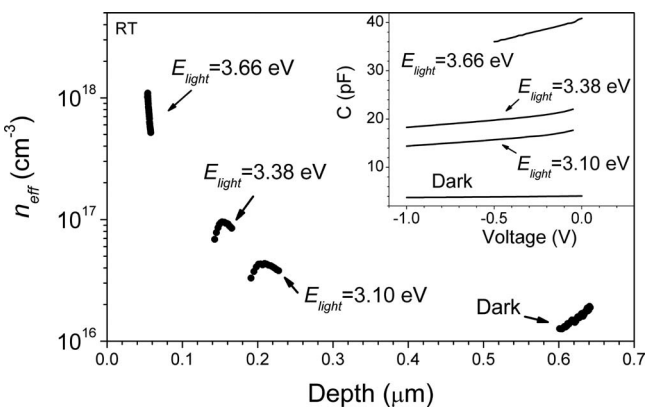

FIG. 4. Effective carrier concentration (n_{eff}) obtained in the $Zn_{0.82}Mg_{0.18}O$ film under different illumination conditions. The inset shows the LCV curves from which n_{eff} was obtained.

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level, the illumination energy to produce its ionization was chosen slightly below the bandgap energy. The resulting trap concentrations are shown in Table I as a function of the Mg content in the layers. The combined trap concentration from all the deep levels found in the bandgap above E_v +580 meV is also shown, and is approximately constant in all samples, suggesting a common physical origin.

Both the E_v+580 and E_v+280 meV deep levels have trap concentration that track the Mg content in the film (Table I). As the Mg content changes from 5.6% to 18.0% the E_v+580 meV trap concentration increases from 1.7×10^{16} to 5.2×10^{16} cm^{-3}, whereas that of the E_v +280 meV level increases quite dramatically from 1.08×10^{17} to 1.01×10^{18} cm^{-3}. This increase in trap concentration for both levels correlates well with the decrease in the net electron concentration with increasing Mg content (Table I). Particularly, and due to its large trap concentration, the E_v+280 meV level seems to be the dominant acceptor level that is responsible for the strong carrier compensation effect observed at high Mg contents. Note that the R_s of the Schottky diodes fabricated on these films increases quite significantly from 4.1 to 3.86×10^3 kΩ as the Mg content is raised up to 18.0% (Fig. 1), effect that can be explained to result by the compensation mechanism discussed above.

This strong carrier compensation effect can also explain why *p*-type doping has conventionally been obtained much more effectively in Mg-containing ZnO films than in pure ZnO.[4–7] Indeed, there are several reports demonstrating *p-n* junctions where $Zn_{1-x}Mg_xO$ is used in the *p*-side, with Mg concentrations in the 10% range.[5,7] The fact that the E_v +280 meV level moves with the valence band edge and that its trap concentration increases with the Mg content can explain why different groups have been able to obtain *p*-type doping using different Mg concentrations. Certainly, Li *et al.*[4] have shown how the increase in Mg content leads to a decrease of the electron carrier concentration and even to an apparent change to *p*-type conduction at ~7% Mg (without intentional doping). In their work, they observe a neutral acceptor-bound exciton for 17% Mg, which assuming the Haynes rule is calculated to be at 212 meV, not too far from the E_v+280 eV level. They assign this level to the (0/-) charge state of the V_{Zn}, calculated in Ref. 12 to be 180 meV in ZnO [the V_{Zn} (-/2-) charge state is calculated to be ~340 meV]. However, Kohan *et al.*[13] calculate transition energies of ~0.3 and ~0.8 eV for the V_{Zn} (0/-) and V_{Zn} (-/2-) defects, respectively, quite different from the previous values. They also predict that the (-/2-) charge state is the most likely V_{Zn} state to be found in *n*-type material grown under O-rich conditions. These discrepancies in energies, together with the fact that theses calculations have been carried out in the binary ZnO, make it hard to identify the origin of the deep levels here reported. Still, and since the films here analyzed were grown under O-rich conditions, the probability of having formed V_{Zn} should be very high.[13] Thus, one could expect the density of V_{Zn} to be high in these $Zn_{1-x}Mg_xO$ films, and that its (0/-) or (-/2-) charge states are related to either or both the E_v+580 and E_v+280 meV levels. Since the concentration of the E_v+280 meV level increases by a factor of 10 for an equivalent change in the Mg content, there is also the possibility that some type of defect complex involving Mg has been formed.

In summary, we have shown that the presence of Mg in $Zn_{1-x}Mg_xO$ can result in the formation of two deep levels at E_v+580 and E_v+280 meV, whose concentrations increase linearly with the Mg content, accounting for the observed decreased in the net electron concentration. The formation of these deep levels and specially the E_v+280 meV ($N_t\sim1\times10^{18}$ cm^{-3} at 18.0% Mg), can explain well the strong carrier compensation effect observed at higher Mg contents, the large series resistance of the Schottky diodes, and is likely at the origin of the amenability to *p*-type doping typically observed in $Zn_{1-x}Mg_xO$.

The work at UPM was supported by MICINN through Project No. TEC2008-04718/TEC.

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