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Investigations of ZnO thin films grown on c-Al$_2$O$_3$ by pulsed laser deposition in N$_2$ + O$_2$ ambient

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ZnO films were deposited on c-Al$_2$O$_3$ using pulsed laser deposition both with and without N$_2$ in the growth ambient. X-ray diffraction revealed poorer crystal quality and surface morphology for one-step growths with N$_2$ in the ambient. A marked improvement in both the crystallographic and surface quality was obtained through use of two-step growths employing nominally undoped ZnO buffer layers prior to growth with N$_2$ in the ambient. All films showed majority n-type conduction in Hall measurements. Post-annealing for 30 min-utes at 600 ºC in O$_2$ systematically reduced both the carrier concentration and the conductivity. A base room temperature carrier concentration of ~ 10^{16} cm^{-3} was linked to Al diffusing from the substrate. 4.2 K photoluminescence spectra exhibited blue bands associated with the growths having N$_2$ in the ambient. Temperature dependent Hall measurements were consistent with N being incorporated in the films. Processed devices did not, however, show rectifying behaviour or electroluminescence.

1 Introduction Considerable effort is currently being made to develop the stable and reproducible p-type doping in ZnO, which is essential in order to realise bright excitonic ultraviolet ZnO Light Emitting Diodes (LEDs) [1-3] and lasers [4]. Amongst the main acceptor candidates (As [5], P [6] and N [7]), N presents the advantages of being better matched to the ZnO lattice plus lower toxicity than As or P, which means that there are fewer handling problems. Hence, N was chosen for the study.

2 Experimental ZnO thin films were fabricated by Pulsed Laser Deposition (PLD) of a sintered ZnO target in O$_2$ ambient with a 248 nm KrF excimer laser, as described elsewhere [8]. Growths were done on c-Al$_2$O$_3$ substrates with and without the introduction of N$_2$ during growth.

Typical film thickness was between 300 and 500 nm. After growth, the samples were subjected to 30 minute anneals at 600 ºC in O$_2$ at varying pressures. Crystal structure was studied using a Panalytical MRD-Pro X-ray Diffraction (XRD) system. Optical properties were studied using above bandgap, photoluminescence (PL) spectroscopy with a 325 nm HeCd laser. Temperature dependent Hall (T-Hall) measurements were made using In contacts in a Van der Pauw configuration. Electrochemical Capacitance-Voltage profiling (ECV) using a 0.1M ZnCl$_2$ electrolyte was conducted using a commercial ACCENT profiler in order to investigate the doping. Secondary Ion Mass Spectroscopy (SIMS) was employed to study the depth profile of Al in the ZnO layers. Samples with nominally diode-like doping were processed into ring mesa LED structures,

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as described elsewhere [9], in order to check for rectifying behaviour and/or Electroluminescence (EL).

3 Results and discussion

3.1 Structural analysis Figure 1 shows XRD $2\theta{-}\Omega$ scans for films grown with N_2 in the ambient both with and without a nominally undoped ZnO buffer layer. The introduction of the high quality buffer layer [10] induced Pendellösung fringes in the $2\theta{-}\Omega$ scan and significantly lower Ω scan linewidths. Thus XRD inferred that the use of nominally undoped ZnO buffer layers yields lower surface roughness and reduced crystallographic dispersion in ZnO overlayers grown with N_2 in the ambient. $2\theta{-}\Omega$ peak position revealed no significant shift in c lattice parameter associated with growth in N_2 ambient.
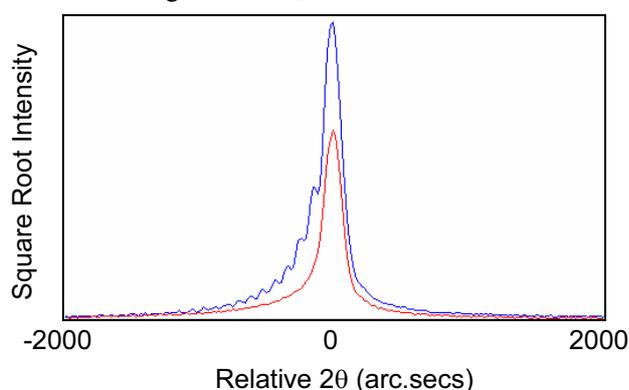
Figure 1 XRD $2\theta{-}\Omega$ scans for the (0002) peak of nominally N doped ZnO grown directly on a) c-Al_2O_3 (lower) and b) nominally undoped ZnO on c-Al_2O_3 (upper).

3.2 Optical characterisation 4.2 K PL spectra for all films showed strong near band edge emission peaked at about 3.356 eV, associated with donor bound excitons. Figure 2 shows deep PL spectra obtained at 4.2 K for films grown with and without N_2 during growth.
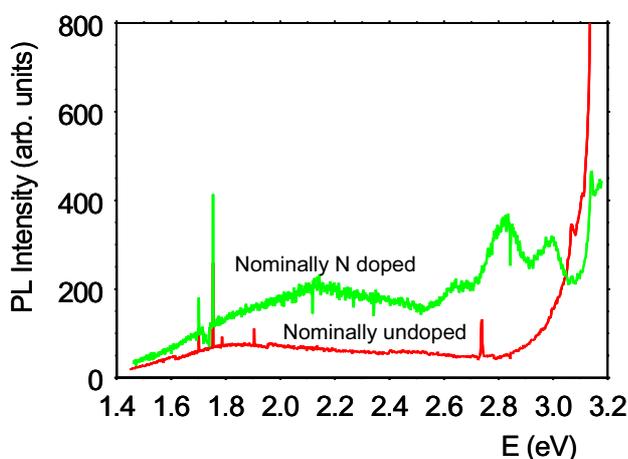
Figure 2 4.2 K PL spectra for nominally undoped and nominally N doped ZnO on c-Al_2O_3

There is a difference in the band structure of the two samples, with yellow (~2.14 eV) and blue (~2.64, ~2.83 and ~2.95 eV) bands appearing in the nominally N doped sample, which are not present in the undoped sample. Such a yellow band is usually associated with defects while the blue bands appear to be linked to the introduction of N.

3.3 Electrical characterisation Room Temperature (RT) Hall measurements show majority n-type behaviour for all films. Annealing in O_2 uniformly reduces carrier concentration (n_c) and conductivity (σ), as would be expected for a reduction in the n–type compensation associated with O vacancies, Zn interstitials and incorporated H [11].

Figure 3 shows results of T-Hall measurements for a nominally undoped ZnO film before and after O_2 annealing at atmospheric pressure.
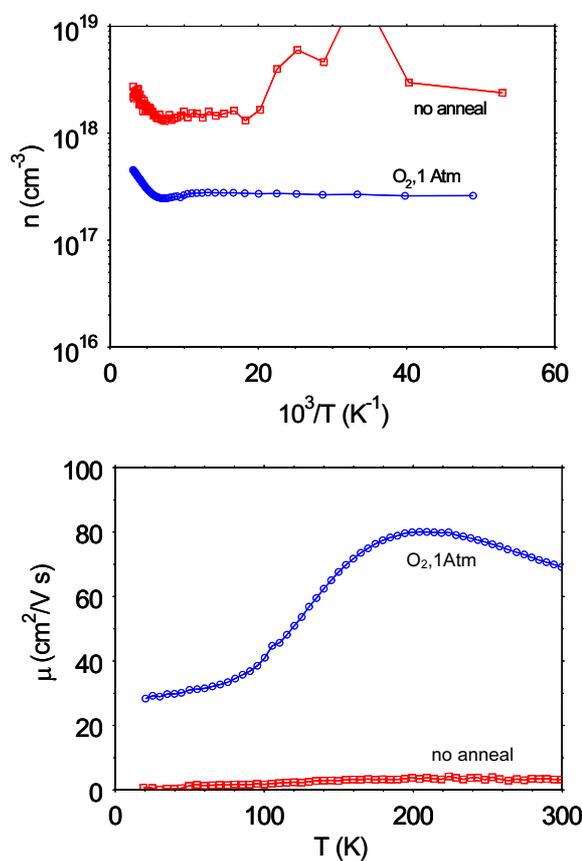
Figure 3 T-Hall measurements of n_c and mobility (μ) for a nominally undoped ZnO/c-Al_2O_3 before and after annealing in O_2.

Hall fitting (including surface effects) for the unannealed sample suggests donor and acceptor concentrations in the low 10^{19} cm^{-3} range and quite strong space-charge scattering in both bulk and surface regions. For the annealed sample, fitting suggests donor and acceptor concentrations in the low 10^{18} cm^{-3} with reduced space-charge

scattering. Annealing in higher O$_2$ pressures reduced the RT n$_c$ to 3×10^{16} cm^{-3}.

Figure 4 shows T-Hall measurements for a nominally N doped film before and after annealing in O$_2$. Hall fitting for the unannealed sample suggests donor and acceptor concentrations in the low 10^{18} cm^{-3} range. This is more compensation than for the nominally undoped sample (as might be expected if N were incorporated). After annealing, the sample exhibited stronger compensation (perhaps indicative of type switching onset).
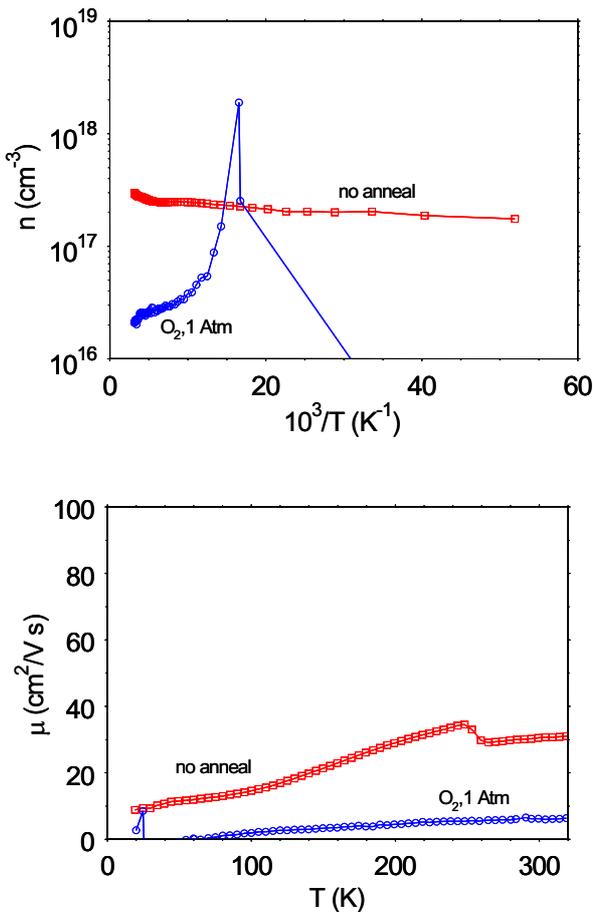
Figure 4 T-Hall measurements of n$_c$ and μ for nominally N doped ZnO/c-Al$_2$O$_3$ before and after annealing in O$_2$.

3.4 ECV profiling The doping was investigated using ECV profiling as the samples had an n-type buffer layer, which influenced the Hall measurements. Furthermore, Hall measurements for ZnO are often reported to be subject to persistent photoconductivity and indiscriminate type switching effects [12]. Also, scanning capacitance microscopy measurements [13] suggest that the distribution of n and p type regions at the surface, in many ZnO layers, may be inhomogeneous and discontinuous, which can give misleading Hall results.

ECV investigations proved ambiguous, however. Measurements for the top surface of all samples indicated majority p-type conduction, while etch points under the surface indicated majority n-type conduction, with a n$_c$ which correlated with that from Hall measurements. Moreover, it was not possible to perform a complete depth profile because the chemical etch rate was too low.

3.5 Compositional analysis Another potential origin of compensation in ZnO is diffusion of the shallow donor, Al, from the c-Al$_2$O$_3$ substrate into the film. SIMS indicated that the Al concentration dropped with increasing distance from the substrate to a residual level of about $\sim 10^{16}$ cm^{-3} for films 400 to 500 nm thick. This n$_c$ corresponds well with those of the Hall studies in films after O$_2$ annealing. Thus the residual donor concentration could be linked to Al in the ZnO layer.

3.6 Devices Nominally N doped layers on nominally undoped buffers were processed into LED structures. No rectifying behaviour or electroluminescence was observed.

4 Conclusion ZnO films were grown on c-Al$_2$O$_3$ by PLD both with and without N$_2$ in the ambient. A nominally undoped ZnO buffer layer was observed to reduce the surface roughness and crystallographic dispersion in the ZnO layers deposited with N$_2$. 4.2 K PL shows blue bands associated with the introduction of N. Hall measurements indicate dominant n-type behaviour for all samples. O$_2$ annealing reduces film σ and n$_c$ down to about 10^{16}cm^{-3}. SIMS shows Al diffusing up from the substrate consistent with such n$_c$. T-Hall measurements are consistent with N incorporation in the ZnO layers grown in N$_2$ ambient but processed devices do not show rectifying behaviour or EL.

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