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# Investigations of p-type signal for ZnO thin films grown on (100) GaAs substrates by pulsed laser deposition

**D. J. Rogers**[1,2*], **F. Hosseini Teherani**[1], **T. Monteiro**[3], **M. Soares**[3], **A. Neves**[3], **M. Carmo**[3], **S. Pereira**[3,6], **M. R. Correia**[3], **A. Lusson**[4,5], **E. Alves**[6], **N. P. Barradas**[6], **J. K. Morrod**[7], **K. A. Prior**[7], **P. Kung**[8], **A. Yasan**[8], and **M. Razeghi**[8]

[1] Nanovation SARL, 103 bis rue de Versailles, 91400 Orsay, France
[2] Université de Technologie de Troyes, 12 rue Marie Curie, BP 2060, 10010 Troyes, France
[3] Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal
[4] Institut d'Electronique Fondamentale, Bât. 220, Orsay University, 91405 Orsay, France
[5] LPSC - CNRS, 1 Place Aristide Briand, 92195 Meudon, France
[6] Instituto Tecnológico e Nuclear, Estrada Nacional 10, Sacavém, 2686 953, Portugal
[7] Physics Department, Heriot Watt University, Edinburgh, EH14 4AS, Scotland
[8] Center for Quantum Devices, Department of Electrical and Computer Engineering, Northwestern University, Evanston, Illinois 60208, USA

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In this work we investigated ZnO films grown on semi-insulating (100) GaAs substrates by pulsed laser deposition. Samples were studied using techniques including X-ray diffraction (XRD), scanning electron microscopy, atomic force microscopy, Raman spectroscopy, temperature dependent photoluminescence, C-V profiling and temperature dependent Hall measurements. The Hall measurements showed a clear p-type response with a relatively high mobility (~260 $cm^2$/Vs) and a carrier concentration of ~1.8 x $10^{19}$ $cm^{-3}$. C-V profiling confirmed a p-type response. XRD and Raman spectroscopy indicated the presence of (0002) oriented wurtzite ZnO plus secondary phase(s) including (101) oriented $Zn_2As_2O_7$. The results suggest that significant atomic mixing was occurring at the film/substrate interface for films grown at substrate temperatures of 450 ºC (without post-annealing).

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**1 Introduction** Arsenic has been proposed by various authors for use in p-doping of ZnO [1–10]. In groundbreaking work, a p-type Hall response was reported for ZnO thin films grown on (100) GaAs substrates using Pulsed Laser Deposition (PLD) [1]. It was suggested that As was the acceptor, and that it diffused from the substrate into the ZnO layer for growths at substrate temperatures ($T_s$) of about 400 ºC and 450 ºC. It was also demonstrated that the p-type response was promoted by post-growth annealing in oxidant ambient at about 500 ºC. In a similar approach [7] a p-type response was also obtained for rf sputtered ZnO/GaAs films after post-annealing at between 400 ºC and 500 ºC. This was attributed, however, to diffusion of Zn into the GaAs rather than p-type doping of ZnO ($Zn_3As_2$ or Zn, for instance, can be p-type [6]). In another attempt to reproduce the original work, plasma-assisted Molecular Beam Epitaxy (MBE) was used to grow ZnO on GaAs, but no p-type response was obtained [5]. Hence, the origin of the p-type response in ZnO films grown on GaAs substrates remains controversial. In this work, we grew ZnO films on GaAs substrates by PLD in order to further investigate this phenomenon.

* Corresponding author: e-mail: DRogers610@aol.com

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**2 Experimental details** ZnO films were grown on semi-insulating (100) GaAs substrates by PLD of a ZnO target with a 248 nm KrF excimer laser. A one step growth at a $T_s$ of 450 °C was performed under $10^{-4}$ Torr of oxygen with a laser frequency of 10 Hz and a substrate target distance of 5 cm. Deposition time was 20 minutes. X-ray diffraction (XRD) was performed using a Panalytical X'Pert MPD diffractometer equipped with a curved graphite monochromator and $CuK_\alpha$ X-ray tube. Atomic Force Microscopy (AFM) was conducted using Digital Instruments Nanoscope IIIA. Scanning Electron Microscopy (SEM) was conducted in a Hitachi S4500. Photoluminescence (PL) measurements were carried out using a He-Cd laser line for above band-gap excitation. A cooled photomultiplier tube was used to detect the emissions in the visible spectral region. The sample was mounted in a cold tip of a cryostat and the temperature controlled from 7K up to Room Temperature (RT). Raman measurements were performed with a Jobin Yvon Spex T64000 using the 514.5 nm line of an Ar ion laser. Hall measurements were made in a four point Van de
r Pauw configuration at both RT and 77 K. Au contacts were sputter deposited onto the film. C-V profiling was conducted, on zones ~1mm in diameter, using $ZnCl_2$ to etch away the ZnO layer.

## 3 Results and discussion

**3.1 SEM, AFM and XRD** SEM images showed a smooth surface with no evidence of holes or particulates. AFM image images (Fig. 1) revealed a 2D/3D Stransky-Krastanov type morphology. SEM of shatter cross-sections indicates that the thickness of the 2D portion was of the order of 70 nm.

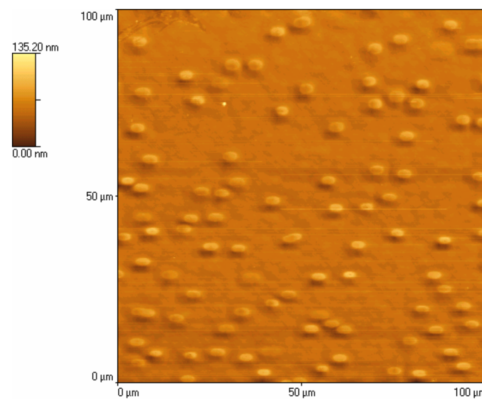


**Fig. 1** Typical AFM image for ZnO/GaAs sample.

Figure 2 shows an XRD θ-2θ scan for the same sample as discussed in Fig. 1. In this spectrum we can identify: a) intense and narrow peaks corresponding to (100) oriented Zinc Blende GaAs, b) broader and less-intense peaks corresponding to (0002) oriented wurtzite ZnO c) a number of very intense and narrow peaks which can be indexed as belonging to (101) oriented Zinc Arsenate ($Zn_2As_2O_7$) - a member of the pyrochlore oxides family d) unidentified peaks at 40°, 86.2° and 124.5° which are broader and less intense than the GaAs peaks. XRD ω scans confirm that the (100) GaAs and the (proposed) $Zn_2As_2O_7$ phase both have very narrow rocking curves, as would be expected for a single crystal. In contrast, the ω rocking curves for the (0002) ZnO, and the unidentified peaks, exhibit larger FWHM as would be expected for phases in a granular thin film with a highly oriented, but mosaic, structure. In view of it's very strong crystal orientation, the proposed $Zn_2As_2O_7$ phase could be explained as the result of atomic intermixing at the film/substrate interface since both As and Ga atoms from the substrate are expected to become mobile at temperatures around 400 °C to 450 °C [7, 8].

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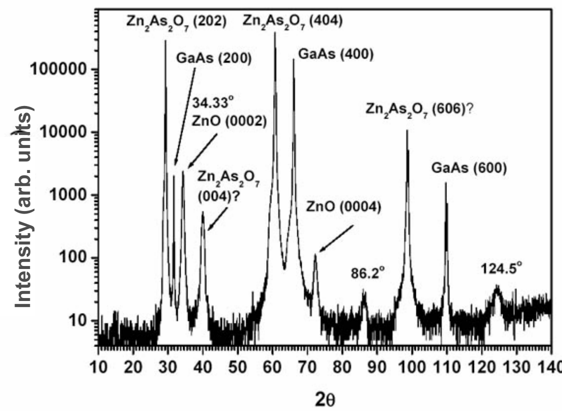


**Fig. 2** Symmetric θ-2θ XRD scan of the ZnO/GaAs sample.

**3.2 PL and Raman spectroscopy** Figure 3 (a) shows temperature-dependent PL under above-band-gap excitation for the same sample as studied in Figs. 1 and 2 above. The emission is dominated by a broad recombination band near 3.0 eV. There is also a weaker and narrower emission line at 3.36 eV, which corresponds to the donor bound exciton spectral region for ZnO. The PL response was observed to be dependent on the laser spot positioning (probably due to macroscopic heterogeneities). Measurements were repeated on the same sample after an interval of several weeks and the PL response was observed to have changed. A similar aging effect has been reported elsewhere for ZnO thin film samples grown on GaAs substrates [11].

Raman measurements were performed at RT using two backscattering geometries: a) $x(\,.\,)\bar{x}$ parallel to growth direction [100] and b) $z(\,.\,)\bar{z}$ , obtained by rotating the sample 90º and focusing the laser on the edge. Figure 3 (b) shows the spectra recorded on the GaAs substrate and on the ZnO thin film. The LO and the TO zone-center optical phonons of GaAs are clearly observed. In the case of the film, the Raman spectra present four peaks located at frequencies not coincident with the expected values for wurtzite ZnO optical phonons. It is possible that these features could be linked to the phase identified by XRD as $As_2O_7Zn_2$ [12].

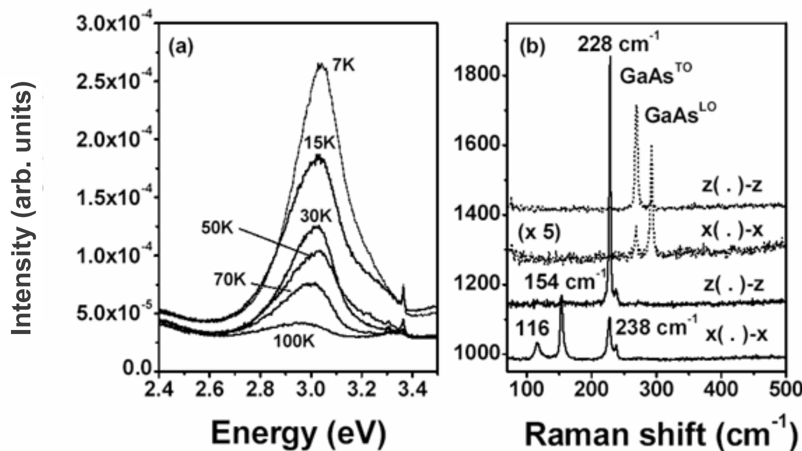


**Fig. 3** (a) Temperature dependent PL spectra of the ZnO/GaAs thin film obtained with above-band gap excitation, (b) RT Raman spectra obtained with the 514.5 nm line of an $Ar^+$ laser: dotted lines - substrate side; full lines – film side.

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**3.3 Hall measurements and C-V profiling** Hall measurements were done at RT and 77 K (Table 1) for the same sample described in Figs. 1 to 3 above. Four separate measurements were conducted so as to check reproducibility. Magnetic field was 0.32T. Carrier concentration was calculated assuming that the 70 nm thick ZnO film was the conductive medium.

**Table 1** Hall measurement data for ZnO/GaAs.

| **Temperature** | **Sheet Resistance ($\Omega$/square)** | **Carrier Type** | **Carrier Concentration ($cm^{-3}$)** | **Mobility ($cm^2$/V·s)** |
|---|---|---|---|---|
| RT | 188 | p | $1.7 \times 10^{19}$ | 267 |
| RT | 190 | p | $1.9 \times 10^{19}$ | 253 |
| RT | 194 | p | $1.8 \times 10^{19}$ | 258 |
| 77K | 257 | p | $3.2 \times 10^{18}$ | 1080 |

At both measurement temperatures the sample showed a dominant p-type response. RT mobility was ~260 $cm^2$/V.s and RT carrier concentration was ~$1.8 \times 10^{19}$ $cm^{-3}$. The mobility is rather high compared with reports of p-type ZnO in the literature. The increase in resistivity with decreasing temperature makes it unlikely that metallic Zn is the origin of the p-type response.
C-V profiling confirmed the existence of a p-type region in the etched zone. The film thickness was insufficient for establishment of a reliable depth profile of carrier concentration and the origin of the acceptors could not be distinguished.

**4 Conclusions** ZnO thin films grown on semi-insulating (100) GaAs substrates by PLD were analysed from the structural, optical and electrical points of view. Certain (as-grown) films showed a clear p-type response in both Hall (RT and 77 K) and C-V profiling measurements. The mobility and carrier concentration were relatively high compared to reports for p-doping of ZnO in the literature. Increased sample resistivity at lower measurement temperature suggested that metallic Zn was not the origin of the p-type response. XRD and Raman studies indicated the presence of (0002) wurtzite ZnO plus secondary phase(s) including (101) oriented $Zn_2As_2O_7$. These results imply that significant atomic mixing was occurring at the substrate/film interface for a $T_s$ of 450 ºC (without post-annealing). The origin of the p-type response remains unclear.

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