Chapter 7

Conclusions

Electrical characterization of process, annealing and irradiation induced defects in ZnO has been successfully achieved using conventional and Laplace DLTS techniques. Conclusions drawn from these studies are given at the end of each section in the results and discussions chapter. In this chapter, the major highlights of the study are briefly stated.

Melt grown ZnO samples have revealed the presence of three prominent point defects, two of which have been explained as being native to the material, i.e. $E1 = E_c - 0.12$ eV and $E2 = E_c - 0.10$ eV. The E3 defect with energy level of approximately 0.30 eV below the minimum of the conduction band has been explained as an extrinsic defect. The identities of these defects are not known yet. E1 and E3 have often been observed in ZnO material grown using different techniques implying they are common to ZnO. The E2 defect has however not been observed in other ZnO material grown using other techniques except in SCVT and MG samples. Thus during material growth and processing, three deep level defects as determined from DLTS are introduced into melt grown ZnO samples.

Results from this study also indicate the effects of the fabrication techniques on the quality of contacts fabricated and the deep level defects introduced into the material. Resistive evaporation techniques yield high quality contacts on melt grown ZnO samples without any deep level defect being introduced during contact fabrication, while the electron-beam deposition technique introduces deep level defects into the semiconductor material with very high concentrations closer to the metal/semiconductor interface. The source of these defects has been explained as possibly due to the ionized heavier gas particles and also stray electrons. This is because the filament is not a true point source of electrons, hence the residual heavier gas particles around and close to the filament area are ionized and are not effectively bent by the magnetic field, hence they end up impinging onto the sample causing damage to the surface.

Annealing of ZnO has proved to be a very significant and crucial step in processing the material for device fabrication. This step provides an avenue for defect engineering in ZnO and possibly a major stride in the realization of p-type ZnO once the optimum conditions for the control of native defects in terms of temperature and ambient conditions have been obtained. This is because the properties of the material and the defects induced during annealing strongly depend on the annealing ambient and temperatures. Annealing of ZnO can also help in understanding and controlling the n-type conductivity in the material. Since ZnO is believed to contain deep states with good colour rendering properties, devices which produce these particular colours can be easily achieved by annealing the material to introduce or activate these states and it is also possible to get rid of unwanted deep level defects through annealing.

Even though annealing has proved to control defects in ZnO (by introducing them and annealing them out), the most important, missing part of the puzzle pertains to the identity, nature and properties of these deep level defects.

Summary of deep level defects observed and characterized in this study

Defect Label	Activation enthalpy (meV)	Capture cross-section (cm^2)	Origin	Identity
E1	110 – 120	$(4 – 7) \times 10^{-12}$	Material growth related	O_i
E2	98 – 100	$(1 – 9) \times 10^{-17}$	Material growth related	?
E3	290 – 310	$(0.7 – 3) \times 10^{-14}$	Material growth related	Transition metal ion
Ex	160 – 180	$(1 – 3) \times 10^{-16}$	700°C Ar Annealed 700°C Ar + O_2 Annealed	?
E4	600 ± 10	$1.4 \pm 0.2 \times 10^{-12}$	Pd e-beam deposition	Oxygen vacancy?
	480 ± 10	$5.0 \pm 0.5 \times 10^{-12}$	Ir e-beam deposition	
	690 ± 10	$1.4 \pm 0.2 \times 10^{-14}$	Pt e-beam deposition	
E4	670 ± 10	$2 \pm 0.2 \times 10^{-11}$	300°C Ar Annealed	?
E4a	680 ± 20	$6 \pm 0.1 \times 10^{-12}$	300°C Ar Annealed	
E4b	590 ± 20	$6 \pm 0.1 \times 10^{-13}$	300°C Ar Annealed	
E4c	500 ± 10	$4 \pm 0.2 \times 10^{-14}$	300°C Ar Annealed	
E4	460 ± 10	$2 \pm 0.2 \times 10^{-14}$	300°C Ar + O_2 Annealed	?
E4a	490 ± 10	$4 \pm 0.2 \times 10^{-15}$	300°C Ar + O_2 Annealed	
E4b	520 ± 10	$6 \pm 0.2 \times 10^{-14}$	300°C Ar + O_2 Annealed	
E4c	530 ± 10	$2 \pm 0.2 \times 10^{-13}$	300°C Ar + O_2 Annealed	
E4	740 ± 20	$2 \pm 0.5 \times 10^{-10}$	400°C Ar + O_2 Annealed	?
E4	540 ± 20	$3 \pm 1 \times 10^{-13}$	500°C Ar + O_2 Annealed	?
E4a	620 ± 10	$3 \pm 1 \times 10^{-13}$	500°C Ar + O_2 Annealed	
E4b	470 ± 10	$3 \pm 1 \times 10^{-15}$	500°C Ar + O_2 Annealed	
E4c	440 ± 10	$2 \pm 0.5 \times 10^{-15}$	500°C Ar + O_2 Annealed	
E4	490 ± 20	$7 \pm 2 \times 10^{-14}$	600°C Ar + O_2 Annealed	?
	600 ± 10	$4 \pm 1 \times 10^{-13}$	400°C O_2 Annealed	
	600 ± 10	$5 \pm 1 \times 10^{-13}$	300°C H_2 Annealed	
	530 ± 20	$1 \pm 0.5 \times 10^{-12}$	Proton irradiation	

E4 refers to the fourth defect observed in the material

Chapter 8

Future Work

Due to the chemical blindness/inability of space charge spectroscopy, the identity of the deep level defects observed and studied in this work is not known yet. Different experiments like ion implantation, positron annihilation spectroscopy, electron paramagnetic resonance, just to mention a few need to be conducted so as to identify the nature and origins of the these deep level defects observed in ZnO. Some of the work that still needs to be performed to get more insight on deep levels in ZnO are:

- Optical DLTS
  -To fully understand the nature and the electronic properties of the E3 deep level.
  - To probe the entire bandgap so as to reveal information of all the annealing induced defects in ZnO.
  - To identify the nature of the annealing induced E4 defect which is assumed to be oxygen vacancy related.
  - To get an idea of how the annealing induced Ex deep level behaves under optical excitation and hence the proof that it is the same as the reported T2 deep level.
- Identify the nature of the electron-beam induced defect by introducing them in a controlled manner
- Perform in-situ annealing and space charge spectroscopy experiments to study the kinetics of each annealing induced defect.
- Since it's proposed that ZnO can be used to fabricate devices that can operate in the UV region and space applications, there is need to perform further annealing studies using different ambient and temperature conditions, to fully understand how devices fabricated on ZnO would perform in highly elevated temperatures.
- Since annealing has proved to increase the acceptor concentration in ZnO, it is important to find a technique of characterizing deep acceptors in ZnO.

- Since annealing has indicated the introduction of deep level defects with high concentrations closer to the surface, surface studies are also required to study the morphology of the surface after annealing the samples.