Chapter 1

Introduction

1.1 Introduction

The research on p-type doping of zinc oxide (ZnO) has gained momentum these days because of the possibility of its application in wide band gap electronic and opto-electronic devices, though synthesis of high-quality and reproducible p-type ZnO remains a formidable technological challenge.

ZnO is a wide band gap semiconductor (E_g = 3.3 eV at 300 K) having large exciton binding energy at room temperature (60 meV at room temperature).

The difficulties of p-type doping can arise from a variety of reasons; viz.

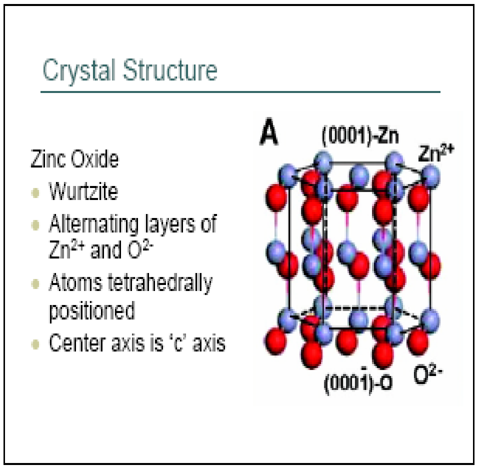
(i) Dopants may be compensated by low-energy native defects, such as zinc interstitial (Zn_i) and oxygen vacancy (V_O),

(ii) Background impurities such as hydrogen (H). H present in the precursor has strong affinity for oxygen (O) so it forms bond with H and thus Zn contributes electrons in ZnO,

(iii) Low solubility of the dopants in the host material, and

(iv) Deep level formation, causing significant resistance to the formation of shallow acceptor level. Deep level impurities are difficult to ionize and thus do not contribute to p-type conductivity.

In order to overcome and to control these limitations, a clear understanding of structural, optical and electrical properties as well as the knowledge on the defects, which originate during doping of ZnO, is necessary.



Crystal Structure

Zinc Oxide
- Wurtzite
- Alternating layers of Zn^{2+} and O^{2-}
- Atoms tetrahedrally positioned
- Center axis is 'c' axis

Fig 1.1 Schematic diagram of crystal structure of ZnO

Synthesis of ZnO with p-type conductivity has been achieved by doping with group I and V elements despite of all difficulties. Dopants, instead of occupying substitutional sites can migrate to interstitial vacancy defect sites in doped ZnO imparting n-type conductivity.

Group-I elements like Li, Na, K on the Zn site act as acceptor but at interstitial site they act as donor that compensate p-type conductivity. But the difficulties arise for substituting Zn in ZnO lattice by group I elements which are:

i) The larger bond length for Na and K than ideal Zn–O bond length induces lattice strain, forms native defects and compensate the very dopants.

ii) Group-I elements tend to occupy the interstitial sites due to small ionic radii rather than substitutional sites resulting in the decay of the acceptors.

Group-V elements (P, As, Sb) other than N on the O site form deep acceptors or donors because of large size difference between dopant and element to be substituted.

1. Both P and As also have significantly larger bond lengths and are more likely to form antisites to avoid the lattice strain.
2. Due to large difference in ionic radii the AX centers (two neighboring bonds are broken, releasing four electrons. However, two of the electrons are recaptured by the two anions to form a strong anion-anion bond) formed by group V dopants convert acceptors into deep donors and are found to be unstable except for P and As [1].
3. To avoid the lattice strain group-V elements generally form antiste resulting in the decay of acceptors.

Thus from above investigation nitrogen can be a better substitutional element among the group-V impurities. The ionic radius of nitrogen is comparable to that of oxygen. Thus it does not form the N_{Zn} antisite, and the AX center if formed is metastable.

However, Look et al. [2] inferred that group-I elements were better substitutional dopants in formation of shallow acceptor levels and thus tend to occupy the interstitial sites due to their small atomic radii, rather than substitutional sites, and therefore, act mainly as donors instead. According to Park et al. [3] substitutional group-I elements form better shallow levels compared to substitutional group-V elements.

Moreover, significantly larger bond length for Na and K (Table 1.1) than ideal Zn-O bond length (1.93 Å) induces lattice strain, increasingly form native defects such as vacancies which compensate the very dopants. These are the causes leading to difficulties in attaining p-type doping in ZnO in terms of shallowness of acceptor levels.

Table 1.1 shows that group-I element can be better p-type dopants than group-V elements as the energy required to form shallow energy level is less.

Table 1.1: The bond lengths, sub levels formed due to doping of different Group I and Group V elements.

	Element	Bond length (Å)	Defect levels formed due to doping relative to VBM* in ZnO
Group I	Li	2.03	0.09
	Na	2.1	0.17
	K	2.42	0.32
Group V	N	1.88	0.4
	P	2.18	0.93
	As	2.23	1.15

* Valence Band Maxima

P-type intrinsic ZnO thin films were deposited on a (0001) sapphire substrate at the optimized temperature of 620 °C by controlling the oxygen pressure of the MOVPE by Ma et al. [4]. They achieved p-type conductivity by adjusting the O partial pressure. Zhang et al. [5] suggested that in both Zn-rich and O-rich conditions the oxygen vacancy, zinc interstitial and zinc vacancy (V_O, Zn_i, Zn_O) have low formation enthalpies so these ‘‘hole killers’’ are abundant and therefore compensate p-type doping in ZnO.

Since susbtitutional impurity gives rise to p-type conductivity, studies on the nature of the defects in doped ZnO is an important area, the knowledge of which is essential in understanding the p-type doping in this material. Another important aspect is the stability of doping on which sufficient data are not available in the literature. With aging, many properties of ZnO are changed and thus the effect of aging on its p-type conductivity is another important area on which investigation can be undertaken. Finally, the efficacy of the p-type doping is best understood by its application. So, devices based on p-type ZnO can be made to study its characteristics.

On the basis of the above discussion the following objectives were identified for the investigation:

(i) Synthesis and characterization of undoped and doped ZnO.
(ii) Doping of ZnO by lithium and nitrogen.
(iii) Structural, optical and electrical characterization of undoped and doped ZnO.
(iv) Pulsed laser deposition of undoped and doped ZnO on different substrates.
(v) Structural, optical and electrical characterization of undoped and doped ZnO films.
(vi) The electrical characterization and understanding of transport mechanisms in undoped and doped ZnO films in the temperature range 10 – 300 K.
(vii) Studies on ZnO based heterojunction for device application.
(viii) Effect of aging on the lithium and nitrogen doped ZnO.
(ix) Positron annihilation spectroscopy of Li and N doped ZnO for the estimation of defects in ZnO.

1.2 References

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