Introduction

Group IV elements like Si and Ge are well established semiconductor materials, but none of them is suitable for optoelectonic applications since they all have an indirect band gap, which does not lead to efficient light emission. Direct wide band gap semiconductors are needed for optoelectronic devices. Such semiconductors are formed mostly from III-V or II-VI compounds. In the last few years, most material developments on wide band gap semiconductors have focused on GaN, ZnSe, and SiC. SiC is an indirect band gap semiconductor. ZnSe based LEDs and laser diodes have a short lifetime due to the formation of defect clusters in the active region. GaN technology is very mature, and high quality devices can be fabricated. However, research on GaN has met many difficulties, for example, in developing high quality films and heterostructures by epitaxial growth. One reason for this is the absence of single crystal GaN wafer for homoepitaxy or small lattice mismatched substrate for heteroepitaxy. Another reason is that high quality films can only be obtained at high growth temperatures, which make GaN more expinsive. II-VI materials, on the other hand, have some interesting properties that do not only enable them to substitute or compliment GaN in several applications, but to also facilitate other applications, for which GaN is not suitable. Due to the large effective mass of electrons in the conduction band and holes in the valence band, as well as the small dielectric coefficient, the excitons in II-VI materials are generally much more stable than their neighboring III-V semiconductors. Therefore, they are more prospective candidate materials in the research on special excitonic properties for both scientific understanding and applications.

Recently, another wide band gap II-VI semiconductor, ZnO has reentered the scientific spotlight, this time as a prospective candidate for optoelectronic and photonic applications at short wavelength. ZnO is a transparent direct band gap (Eg = 3.37 eV) material with the wurtzite lattice structure. It has attracted much attention in recent years due to its fascinating properties which were discovered in 1970s, but cannot be employed at that time for opts-electronics due to luck of the suitable epitaxial technology. ZnO is often compared to GaN because of their nearly the same band gap needed for ultra-violet or blue light emission. Besides this major similarity, ZnO has a number of advantages that include extremely stable excitons. From the viewpoint of productive application, ZnO holds a few superiorities compared with GaN. Unlike GaN, ZnO can be grown in bulk and can be used as its own substrate. One of the main raw materials like: A few types of efficient, clean and low-cost oxygen sources are available for ZnO epitaxial growth, such as H_2O vapor, H_2O_2, ozone,

alcohol and oxygen radical. The growth temperature for ZnO (typical 500°C) is much lower than that of GaN (usually 1000°C). A low growth temperature is advantageous to the fabrication of quantum structures (needed for efficient light emission) as it suppresses inter-diffusion at hetero-interfaces and non-uniform nucleation in alloy region. A low growth temperature also facilitates the incorporation of dopant and alloy constituents by suppressing the segregation effect. Since ZnO itself is a nontoxic material, no toxic materials are needed for its growth. In addition to these technological advantages, ZnO is highly radiation resistant making possible ZnO-based devices interesting for space applications. Due to its high melting point and large cohesive energy amongst the II-VI semiconductors, it is expected that a degradation of the material due to the generation of dislocations during device operation will be reduced. The most interesting property of ZnO is the large exciton binding energy of 60 meV, which is almost two times larger than either GaN or ZnSe. This is one of the key parameters that enable UV laser diodes and other exciton-related light emitting devices to be operated even above room temperature. By incorporating transition metals such as vanadium, manganese, cobalt in ZnO, a diluted magnetic semiconductor (DMS) could be obtained. Alloying ZnO films with MgO or CdO potentially permits the band gap to be controlled between 2.8 and 4 eV and even higher, which facilitates band gap engineering [1], while the lattice constant does not deviate much from that of ZnO, which smaller in-plane lattice mismatch than the (Al, Ga, In)N system in the same range of bandgap and lattice constant. The strong point of ZnO is, somehow, a combination of the good features of both GaN and ZnSe, which make ZnO an ideal candidate for a variety of devices including blue and ultra-violet laser diodes and light emitting diodes.

During the pereceding years, thin film growth techniques, such as sputtering and chemical vapor deposition, have been developed for ZnO growth. However, at that time, ZnO was thought to be used as a piezoelectric material, or transparent conductive material, for the applications to such as SAWDs, transparent electrode for solar cells, rather than a semiconductor. For these applications, the high crystal quality has never been a critical issue, so that, ZnO is still far from the stage for optoelectronic application. Molecular beam epitaxy (MBE) needs to be investigated as a reliable tool for the growth of highly crystalline ZnO. MBE has some substantial advantages over previous vacuum deposition techniques, such as hotwall epitaxy, which are the ultra-high vacuum (UHV) environment and significantly more precise control of the beam flux and growth conditions. In contrast to other epitaxial growth techniques, such as liquid phase epitaxy and vapor phase epitaxy, which proceed at nearly thermodynamic equilibrium conditions and are controlled by diffusion processes at the solid

and liquid (gaseous) phase boundaries, in MBE, epitaxial growth is governed mainly by the kinetics of the surface processes occurring when impinging beams react with the outermost atomic layers of the substrate crystal. This is far from the thermodynamic equilibrium conditions, although a thermodynamic approach can be applied to MBE growth description. In comparison to all other epitaxial growth techniques, MBE has a unique advantage. Being realized in UHV environment, it may be analized and controlled in situ by surface diagnostic methods, such as reflection high-energy electron diffraction, Auger electron Spectroscopy. These powerful facilities for analysis and control eliminate much of the guesswork in MBE, and enable the fabrication of sophisticated device structures using this growth technique. These advantages make MBE a state-of-art epitaxial growth technique with excellent flexibility.

The aim of this work is thus to develop an epitaxial growth technique, which should be able to fabricate device-quality ZnO thin films. Nitrogen-doped ZnO will investigate. The ZnMgO based quantum structures with well controlled Mg content are also to be studied.Therefore, MBE as an epitaxial growth technique and a widely used low-cost sapphire substrate are chosen as the technical basis for this research. Furthermore, the possibility of device fabrication on the basis of ZnO and ZnO-based heterostructures is to be analyzed by fabricating and characterising device structures.

In this thesis, the research background and the fundamental material properties will be presented in chapter 1. In chapter 2, attention will be given to MBE growth facilities and the characterization methods involved in this work. Chapter 3 treats experimental processes of the growth of ZnO and ZnMgO epilayers on different substrates (GaN template, c-sapphire and ZnO), using different oxygen precursors (oxygen plasma and hydrogen peroxide), and the subsequent structural, optical and electrical characterisation of the obtained layers. P-type doping and devices based on ZnO will be a subject of chapter 4. ZnO-based Heterostructures for Opto- & Magneto-electronics will be considered in chapter 5. Finally, conclusions and critical analysis of the obtained results are presented in chapter 6.