1 Introduction

Unique properties of ZnO as a semiconductor make this material very promising for utilization in technology of optoelectronic devices. A direct band-gap of about 3.37 eV and a possibility of its engineering by doping ZnO with Mg or Cd open the access to the ultraviolet spectral region. Although light emitting and laser diodes for such short wavelengths have been already realized on the basis of GaN semiconductor compound, there are still some advantages of ZnO comparing to GaN. First of all, ZnO has very stable excitons with the binding energy of 60 meV which is twice higher than in GaN. This makes it possible to obtain exciton-polariton-coupling even at room temperature. Moreover, ZnO is very stable against radiation and promises higher lifetimes for the devices based on it. An additional and very important advantage of ZnO is a principle possibility to produce ZnO bulk substrates with a high crystal quality by the hydrothermal method, although the resulting substrates are very expensive and the process is still in optimization. Lattice-mismatched sapphire substrates have been used for a long time as a cost-effective alternative to bulk ZnO substrates. Heteroepitaxial layers with a relatively high crystal quality have been achieved.

The main obstacle in ZnO-material technology is the realization of a reliable p-type doping. A lot of efforts have been done lately in order to overcome this problem. Different doping elements from groups I and V of the periodic table have been implied in different technological processes like diffusion, epitaxial growth by molecular beam epitaxy or metal-organic vapor transport and ion implantation. Many works have been published claiming to succeed in p-type doping. Unfortunately, there have been no reports with reproducible results and a lot of publications on p-type ZnO without electroluminescence measurements have appeared. It is clear that one has to understand the defect dynamics in this material to figure out why the impurities that theoretically should act as acceptors could not induce any conduction type conversion. A correct interpretation of transport measurements is a possible way to the solution of such tasks.

The main emphasis of this work is the investigation of electrical properties of ZnO thin films grown by molecular beam epitaxy, undoped and doped with nitrogen. An accurate analysis of temperature domain Hall-measurements and electrochemical C-V-profiles has been a tool in this research. The second chapter in this manuscript gives a short overview on material properties of ZnO, the third one - on characterization methods and molecular beam epitaxy. Further the electrical properties of heteroepitaxial ZnO thin films are discussed in the fourth chapter. A physical model of the temperature dependencies of the electron mobility and carrier concentration in such layers have been explored. Attempts to optimize the heteroepitaxial growth in order to produce p-type ZnO samples are also discussed in the section. The fifth chapter compiles results on homoepitaxial growth and characterization of the obtained layers. The sixth section summarizes all the data that have been gathered during this research on p-type doping of ZnO by molecular beam epitaxy.

2 Crystal properties of ZnO and basics of carrier transport

Basic material parameters and physical models of charge carrier transport are presented in this chapter. Besides lattice geometry and band structure, there is also such an important issue as intrinsic point defects. Their electrical activity and formation energy are described here. A short overview of possible configurations of dislocations is also given here since some types of these one-dimensional defects have an immense influence on the carrier transport properties of ZnO. A doping feasibility of this compound material with extrinsic elements, charge statistics and scattering processes encountered in ZnO are discussed in this section as well.

2.1 Crystal structure of ZnO

There are three possible ways of ZnO crystalisation: with zinc-blende, rocksalt and wurtzite symmetry [1,2]. First two crystal structures are instable and exist in specific conditions. Zinc-blende structure can be achieved only by growth on substrates with cubic crystal symmetry and rocksalt ZnO - only under extremely high pressures. In contrast, the wurtzite ZnO

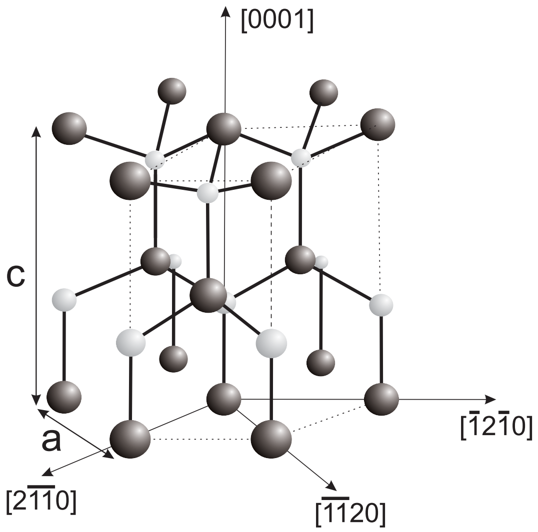

Figure 2.1: Wurzite Lattice. The black spheres represent zinc atoms and white - oxygen ones.

structure is stable in ambient conditions. This kind of crystal geometry is presented in Fig. 2.1. The gray spheres represent a zinc atom and white - oxygen ones. As it can be seen, each atom is surrounded by four atoms of another element. This configuration is governed by covalent bonding, but there is also an ionic bonding in ZnO crystal. The covalent bonding is denoted by solid lines and ionic - by dashed ones in Fig. 2.2. This picture shows that wurtzite crystals have AaBbAaBbAaBb... stacking sequence along the [0001]-axis. The lattice parameters of ZnO are as follows: a=3.250 $\AA$, c=5.204 $\AA$, u=0.382, where u represents an internal parameter and uc describes the length of the bonds parallel to [0001] (c-axis) [2].

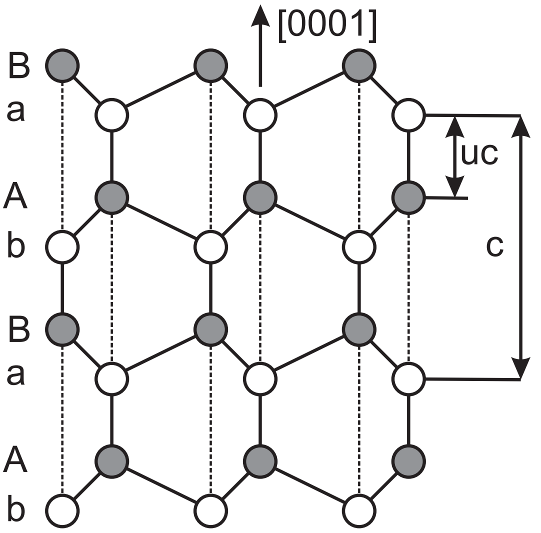

Figure 2.2: Stacking sequence of wurtzite lattice

Due to the specific features of the crystal structure of ZnO bulk specimens, it can be distinguished between two types of surfaces in basal plane (perpendicular to c-axis): Zn-terminated or (0001)-surface and O-terminated or $(000\overline{1})$-surface. These surfaces have different properties which are described by the surface bonding model [3]. As one can see in Fig. 2.3, the atoms on the surfaces are triply bonded and the oxygen atoms have a dangling bond with two electrons on the surface. These dangling bonds govern the difference between O-terminated and Zn-terminated faces of ZnO-bulk crystals during such processes as wet-chemical etching and homoepitaxial growth. These effects will be shown in the experimental chapters of this work. At that point, the most important structural properties necessary for further discussions are described.

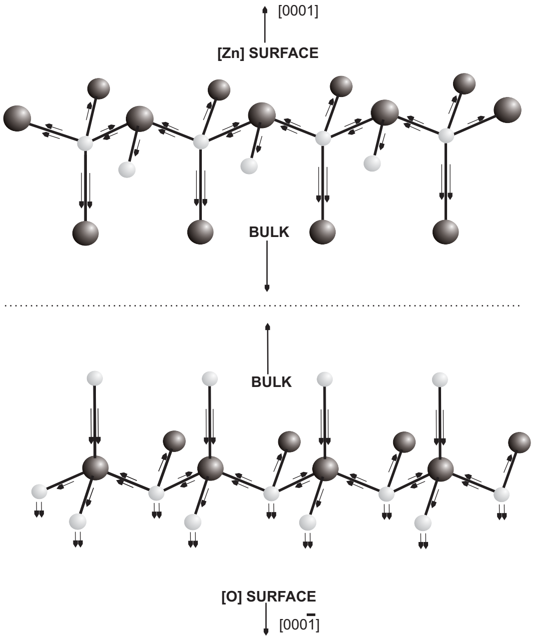

Figure 2.3: Polar faces of ZnO lattice

2.2 Electronic band structure

ZnO is a direct band gap semiconductor. Its full band structure is not discussed in this work. Fig. 2.4 schematically represents instead the band structure in the vicinity of the so-called Γ-point. This is the most important area in the dispersion diagram because all the charge-transport and optical processes occur in the region of the energy minimum. The valence band is split by crystal field and spin-orbit interaction into three states. These are shown in Fig. 2.4 and denoted by the letters A, B and C [4]. The notation Γ_7, for example, describes the symmetry of a state. The energy gap E_g at T=1.6 K equals 3.437 eV. The energy spaces between states in the valence band are as follows: ΔE_{ab}=4.9 meV and ΔE_{bc}=43.7 meV. The temperature dependence of the energy gap is expressed by the formula:

$$E_g(T) = E_g(0) - \frac{\alpha \cdot T^2}{T + \beta}, \tag{2.1}$$

where $E_g(0)$=3.38 eV, α=9.00·10^{-4} eV/K and β=2.23·10^3 K [5]. The band gap can also be modified by substitution of Mg (for widening) or Cd (for narrowing) at the place of Zn-atoms in the lattice. Further in this work, the ternary $\mathrm{Zn}_{1-x}\mathrm{Mg}_x\mathrm{O}$ compounds only will be described. The resulting band gap depending on the Mg content in such structures can be expressed as [1]:

$$E_g(x) = (1 - x) \cdot E_{ZnO} + x \cdot E_{MgO} - b \cdot x \cdot (1 - x), \tag{2.2}$$

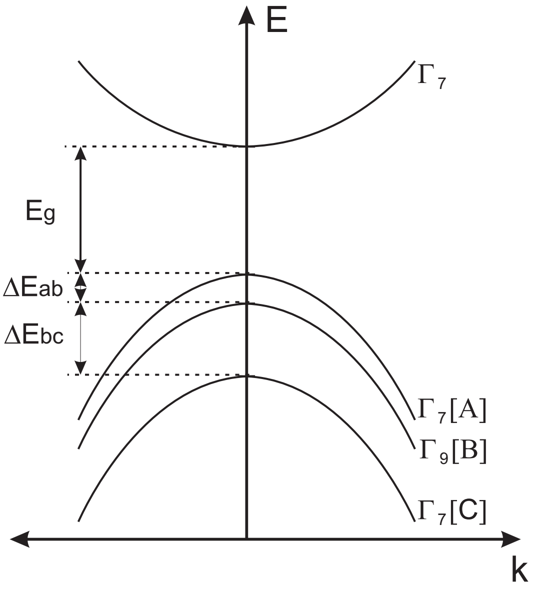

Figure 2.4: Electronic band structure of ZnO

where b is a bowing parameter. The energy gap of MgO is about 7.7 eV and of ZnO - about 3.3 eV. The resulting energy gap increases linearly with Mg content up to ≈ 4.15 eV for $x \leq 0.36$. This means that the bowing parameter equals zero in this range. Further increase of x results in a metastable ternary structure with a cubic lattice and a band gap of up to 5 eV. The solubility of Mg in ZnO-lattice saturates causing segregation of MgO in this case.

2.3 Intrinsic point defects

Intrinsic point defects are a very important issue in semiconductor technology because they influence electrical properties of a material system. Knowledge of the point defects formation dynamics provides control on the quality and functionality of semiconductor devices. This is exactly the case for ZnO material system. Intrinsic point defects which act as donors in this compound material are the potential candidates for p-type doping "killers". The donor-type defects in ZnO are oxygen vacancies (V_O), zinc interstitials (Zn_i) and zinc antisites (Zn_O). The acceptor-type defects are zinc vacancies (V_{Zn}), oxygen interstitials (O_i) and oxygen antisites (O_{Zn}). Geometries and specific properties of these defects can be found in reference [6]. In this work a short overview on important features of the point native defects is given.

Oxygen Vacancies. This type of defect has the lowest formation energy among the donor-type defects. It has three states: doubly ionized, singly ionized and neutral. Doubly ionized and neutral states are the most stable. This defect has been shown to be a rather deep donor than a shallow one. It has a quite high formation energy for Fermi-levels near the conduction-band minimum (n-type material). This is the case even under Zn-rich conditions. Its concentration will be always low and that is why the ZnO unintentional n-type conductivity can not be caused by this type of defect in equilibrium conditions. The formation energy of V_O decreases with lowering Fermi-level, which indicates that oxygen vacancies could be a reason for compensation of p-type doping in ZnO.

Zinc interstitials. There are two types of Zn_i in ZnO-lattice: the tetrahedral and octahedral sites. The octahedral site is very stable and consists of a Zn-atom in interstitial channel along the c-axis. This defect can be presented in its charge-state of 2+ and it has a very high formation energy in n-type material as well. This formation energy decreases with lowering Fermi-level. It makes Zn_i to be a potential candidate for a p-type compensating defect.

Zinc antisite. Zinc antisite is a native point defect which can act as a shallow donor with its stable charge state of 2+. It represents a zinc atom at the place of an oxygen one in the lattice. The formation energy of this defect is very high for any Fermi-levels in equilibrium conditions.

Zinc vacancies. Zinc vacancy is a rather deep acceptor point defect. It is more favorable to form in n-type ZnO under O-rich conditions in a 2- charge-state. It acts as a compensating center. It has the lowest formation energy of all the possible point defects in n-type material. In contrast, its formation energy is very high in p-type ZnO.

Oxygen interstitials. There are three types of oxygen interstitials: octahedral, tetrahedral and split interstitials. An oxygen atom at the tetrahedral site is unstable and relaxes into a split-interstitial configuration where it shares a lattice site with the nearest neighboring oxygen atom. This configuration is electrically inactive. An oxygen interstitial can be electrically active and show acceptor character if an oxygen atom occupies the octahedral site. In p-type and semi-insulating material oxygen interstitials would exist in their neutral state in the form of split-interstitials. In n-type material they are presented as doubly ionized deep acceptor centers at the octahedral sites. In both cases formation energies are very high except for extreme O-rich conditions.

Oxygen antisites. This defect is formed by an oxygen atom wrongly occupying Zn-sublattice. It has an acceptor character but it is very unfavorable to form even under O-rich conditions. It can be produced in non-equilibrium conditions. These could be, for example, ion implantation or irradiation. The ideal configuration where oxygen takes exactly a Zn-site is unstable and it relaxes into the off-site geometry.