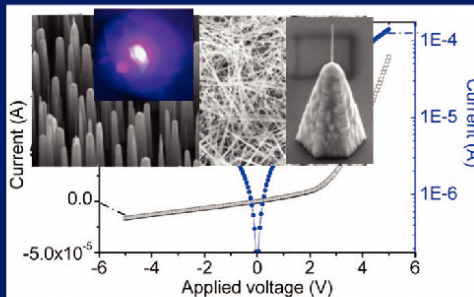




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**Fabrication and Characterisation of Device Quality
ZnO Nanostructures**

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1. Introduction and motivation

In the past decades, increasing demand in the performance and scope of semiconductor-based devices like transistors, light emitting devices, actuators, sensors has led to a tremendous increase in device density. This is in conformity with the prediction of Gordon E. Moore [MOO65], in which he envisaged an exponential increase in the number of transistors, say in a computer processor. He later estimated that this exponential increase in the number of electronic devices on chips would reach its physical limit by 2017 [MOO97]. This exponential increase in device density is accompanied by a continuous miniaturisation of devices down to the nanometer scale. With the example of a conventional electron device like the transistor, the continuous reduction in the width of its gate or base in order to increase its aspect ratio and hence reduce transient time makes quantum-mechanical effects like tunnelling inevitable, when the size of such device components approaches the electron wavelength. It thus becomes complicated to understand unusual device behaviours. In order to meet future demands for performance of microelectronic, optoelectronic, micromechanic etc. chips, nanoscale devices are inevitable. They are suitable because their size will be taken into consideration when establishing their functionality on the basis of the properties of the nanostructures used for their fabrication. Good nanoscale devices will therefore be realisable only on the basis of good quality nanostructures, for which special *nanomaterials* including zinc oxide (ZnO) are indispensable. In order to understand the behaviour of nanodevices, it is important to understand how far the material properties at the mesoscopic scale can be related to those at sub-micron level or nanoscopic scale. The only reliable way to understand the material properties at submicron level is to fabricate and characterise them, comparing their properties with those of layers and bulk materials. As opposed to semiconductor epitaxial layers, epitaxial nanostructures are expected to possess high crystalline quality since their small contact area on the substrate reduces the probability of defect formation during their fabrication. While being expected to serve in understanding the dependence of some physical effects on the size of the material in question and as functional units for electronic, optoelectronic, spin-electronic, micromechanical, electrochemical and even biological devices, one dimensional nanostructures could also serve as interconnects in integrated device systems.

Recently, oxide semiconductors have attracted significant attention as the basis of smart and functional materials due to two fundamental structural characteristics: they have cations with mixed valence states and anions with deficiencies [DAI03]. By varying any of

these characteristics, the electrical, optical, magnetic, chemical properties of the oxide semiconductor can be tuned. ZnO is a wide and direct band-gap ($E_g = 3.37$ eV) transparent II-VI oxide semiconductor with a large family of nanostructures (nanorods, nanowires, nanocombs, nanobelts, nanobows, nanohelices etc.). It has attracted much attention in recent years due to its fascinating properties. Its large exciton binding energy of 60 meV guarantees stable excitons even above room temperature [HLI06] and makes ZnO even more promising for ultra-violet light emission and detection than its III-V counterpart, GaN with an exciton binding energy of only 20 meV. High quality ZnO nanostructures are expected to exhibit good optical properties suitable for light-emitting devices (light-emitting diodes and laser diodes). Amongst its nanostructures, ZnO nanorods and nanowires are more promising because of their relative ease of formation and device fabrication. Nanorods with high aspect ratio would find application in field emission that is extendable as electron source for flash memory, electron microscopy, field emission displays and also micro-electro-mechanical systems (MEMS). Wang et al demonstrated that the current flowing through cadmium-doped ZnO nanowires increased by three orders of magnitude when exposed to moist air with humidity of 95% [WAN04], thus indicating how ZnO nanorods could be used for gas sensing. By incorporating transition metals such as vanadium, manganese, cobalt in ZnO, a diluted magnetic semiconductor (DMS) could be obtained. Such a semiconductor with ferromagnetic properties is highly needed in the field of spin-electronics (*spintronics*), in which the spin degree of freedom of the electron is exploited in conjunction with its charge for new and ultra-fast class device applications. Ferromagnetic ZnO nanorods could serve for example, as channels for spin transport to study the newly proposed Datta-Das spin field-effect transistor [DAT90]. The chain of applications of ZnO nanostructures could be extended through solar cell fabrication to the employment of their powder-form for pigments and protective coatings, for example, on metals and in sun creams to protect the skin from ultra-violet radiation from the sun. These applications require an efficient but low-cost fabrication of high purity nanostructures.

There are basically two fabrication approaches for semiconductor nanostructures: the top-down approach that is realised through lithography and etching techniques, and the bottom-up approach, which is mainly crystal growth. The latter potentially leads to better quality nanostructures and thus attracts much attention. In most cases, a catalyst such as gold, platinum etc. is used to initiate the growth of nanostructures. Many semiconductor growth methods like molecular beam epitaxy (MBE), metal-organic vapour phase epitaxy (MOVPE), pulsed-laser deposition (PLD), and physical vapour transport (PVT) are limited by their

inability to provide a growth window for high quality nanostructures. They thus employ catalysis, which together with non-elemental sources present a source of impurity. In addition, these methods are expensive and would be very costly for industrial production.

The aim of this work is thus to design and implement a vapour transport system for the growth of high purity ZnO nanostructures (nanowires and nanorods). To demonstrate their good quality, the eventually obtained nanorods are to be extensively characterised with respect to their crystalline quality, optical and electrical properties. Also, the incorporation of transition metals in ZnO is to be investigated with respect to the kind of magnetic coupling. Furthermore, the possibility of device fabrication on the basis of fabricated nanostructures is to be analysed by fabricating and characterising device structures.

In this dissertation, a closer look at ZnO, its properties and nanostructures will be made in chapter 2, while chapter 3 treats the developed vapour transport system together with other growth and characterisation methods involved in this work. Chapter 4 handles experimental processes on the fabrication of ZnO nanostructures on different substrates and the subsequent characterisation of the obtained nanostructures. Magnetism and hence the incorporation of transition metals in ZnO and more particularly in ZnO nanorods will be dealt with in chapter 5. Finally, the fabrication of some nanorod-based device structures will be the subject of chapter 6. A critical analysis of the entire work vis-à-vis the obtained results will follow as summary in chapter 7.

2. ZnO as a semiconductor and nanomaterial

Although ZnO has recently attracted much interest in semiconductor research, it had long been identified as an interesting semiconductor material. Early investigations on its crystal structure date back to 1935 [BUN35]. Many other research works followed in the next four decades to understand other properties (optical, electrical etc.) of ZnO [MOL54, MEA65, DAM66, GAL70]. The greatest difficulty so far is the production of high-conductivity p-type ZnO, which is necessary for functional electronic and optoelectronic devices [LOO04]. Megneto-electronics, micromechanics are other areas in which ZnO finds application as semiconductor with additional material properties. There are however, several applications of ZnO, for which the p-n junction and also high crystalline quality material are not needed. ZnO finds applications in the rubber industry as a catalyst in vulcanisation processes, in the cosmetic industry since it has antibacterial properties, and even in sensing, where nanostructures of ZnO seem very promising.

In this chapter, the main material-specific properties of ZnO that are relevant for semiconductors shall be presented, followed by an introduction to nanostructures of ZnO, how they are fabricated and potential application areas.

2.1 Properties of ZnO

2.1.1 Crystal and band structure of ZnO

Like many other II-VI semiconductors, ZnO crystallises in the cubic zinc-blende [ASH00] or the hexagonal wurtzite crystal structure. The rocksalt crystal structure has also been reported for ZnO [REC98]. In each of these structures, each anion (O^{2-}) is bonded to four cations (Zn^{2+}) that form the corners of a tetrahedron, common with sp^3 covalent bonding. ZnO also exhibits ionic behaviour with its ionicity somewhat between a covalent and an ionic crystal. Theoretical calculations by Jaffee and Hess of the cohesive energy per O-Zn bond suggest that the wurtzite structure of ZnO is the most thermodynamically stable phase [JAF93]. Table 2.1 shows the calculated values in comparison with experimental results deduced from the enthalpy of formation of ZnO [ÖZG05]. The largest enthalpy of formation of the wurtzite structure corresponds with theoretical results and confirms that the hexagonal wurtzite is the most probable crystal structure of ZnO at ambient conditions.

The atomic arrangement in the ZnO wurtzite crystal lattice is depicted in Figure 2.1. This crystal lattice exhibits hexagonal symmetry and has the stacking sequence ABA-BAB... whereby A, B comprises 2 levels of similar ions (O^{2-} or Zn^{2+}). Its a - and c -axis are perpendicular to each other.

Table 2.1: Calculated and experimental values of cohesive energy in Zn-O bond

	Zink-blende	Wurtzite	Rocksalt
Calculated(eV)	-5.606	-5.658	-5.416
Experimental (eV)	-7.679	-7.692	-7.455

The a lattice parameter is the distance between two neighbouring Zn atoms on the C-plane while the c lattice parameter is the distance between two neighbouring Zn atoms on the A-plane, as shown in Figure 2.1. The O-Zn bond length is 0.197 nm [DES98] and the lattice parameters take the values $a_0=0.325$ nm and $c_0=0.5204$ nm at ambient conditions [KAR96].

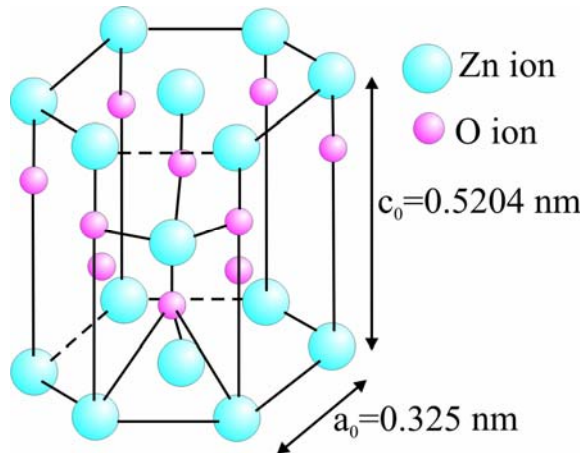


Figure 2.1: The hexagonal wurtzite structure of ZnO crystal

Due to its anisotropy, the ZnO crystal shows polar behaviour. It can be terminated with Zn ions in the (0001) direction or with O ions in the (000-1) direction. Since the O-terminated surface is more quickly etched than the Zn-terminated surface [GRU03], the polarity of a ZnO wafer or crystal sample can be identified.

The symmetry of hexagonal ZnO and its direct band gap facilitates the explanation of its properties that are determined by its band structure using the Γ point ($\vec{k} = 0$) of the Brillouin zone (Figure 2.2a). There, the deepest conduction band arises through unoccupied $4s$ orbitals of the double-ionised Zn atom (Zn^{2+}), while the topmost valence band arises through occupied $2p$ orbitals of O^{2-} . From the crystal symmetry $C6v$ of ZnO, the conduction band has Γ_1 symmetry [RÖS69]. Due to spin-orbit splitting, the valence band obtains the Γ_7 symmetry. Due to its p -state, the valence band has both the Γ_1 and Γ_5 symmetries with six-fold

degeneration. This degeneration is outweighed through crystal field and spin-orbit splitting, so that the valence band consists of three sub-bands, Γ_7 , Γ_9 and Γ_7 commonly called A, B and C valence bands. The assignment of these bands to the different symmetries is

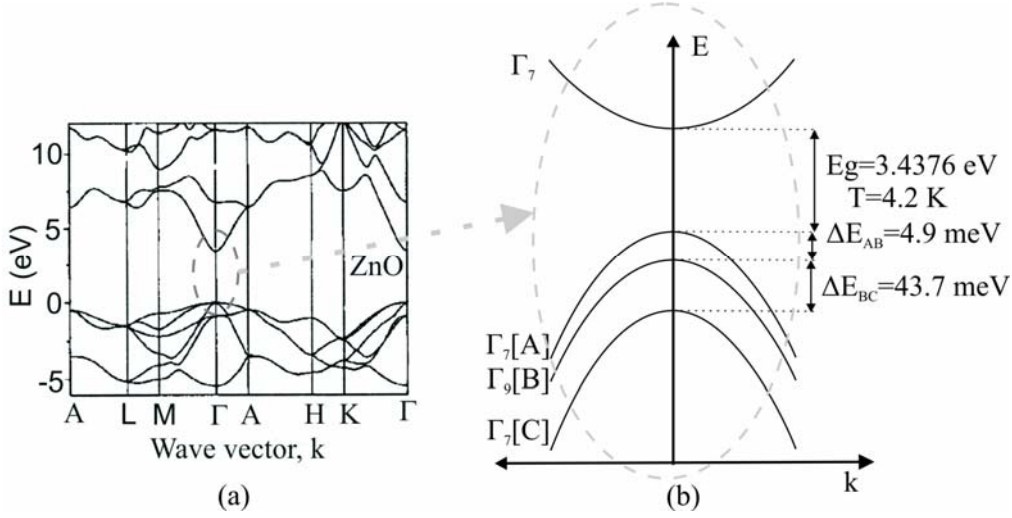


Figure 2.2: *Electronic band structure of ZnO after [FAN06] and a closer analysis of the Γ point after [MEY04]*

controversially discussed. The latest studies assign them as Γ_9 (A), Γ_7 (B) and Γ_7 (C) [REY99], B. Meyer et al reported on the order Γ_7 (A), Γ_9 (B) and Γ_7 (C) [MEY04]. The band gap energy of ZnO thus depends on the valence band in question as can be seen in Figure 2.2b

2.1.2 Other physical properties of ZnO

Besides the crystal and band structures of ZnO, a few determinants of its mechanical and temperature stability, like its melting point and its bulk modulus will be discussed in comparison with those of its III-V counterpart, GaN and the most popular semiconductor material, Si. This will be followed by some basic electrical properties of ZnO.

The bulk modulus measures the response in pressure due to a change in relative volume, essentially measuring the substance's resistance to uniform compression. The bulk modulus B of a hexagonal crystal can be determined from four independent elastic constants, C_{11} , C_{12} , C_{13} , C_{33} as [ÖZG05]

$$B = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}} \quad (2.1)$$

The Young modulus E , which is a measure of the elasticity or stiffness of a given material and the shear modulus G that describes a material's rigidity are defined as

$$E = \frac{3B}{1-2\nu} \quad \text{and} \quad G = \frac{E}{2(1+\nu)}, \quad (2.2)$$

where ν is the Burger's vector. ZnO has a bulk modulus of 133.7–183 GPa, while GaN and Si have bulk modulus of 190–245 GPa and 98 GPa respectively. Since E and G are directly related to B it is obvious that ZnO is much harder and more resistant to deflection or deformation by an applied force than Si.

ZnO is known to have the strongest piezoelectric response amongst all tetrahedrally bonded semiconductors [COR94]. The calculated piezoelectric constant of ZnO is about 1.3 C/m^2 [WU05,XIA06]. Lithium niobate, for example, that is referred to as a transducer crystal has a piezoelectric constant of 1.8 C/m^2 . This shows that ZnO could be employed for applications requiring large electromechanical coupling. The electrical properties of ZnO, like any other material, greatly depend on the material quality. So far, the largest reported electron mobility for ZnO is $205 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for an electron density of $6 \times 10^{16} \text{ cm}^{-3}$, although theoretical calculations using Monte Carlo simulation predict an electron mobility of up to $300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [ALB98]. As compared to Si, GaAs, InP and its III-V counterpart GaN, ZnO possesses a much less electron mobility, thus making it less competitive for high-speed electronic devices, except otherwise doped with other materials.

2.1.3 ZnO-based ternary semiconductors

Similar to well-known material systems like GaAs, InP and even ZnSe, the semiconducting properties of ZnO can be altered by introducing metal atoms that will partially substitute Zn atoms in the crystal lattice and thus influence its band gap, electron and hole mobility,

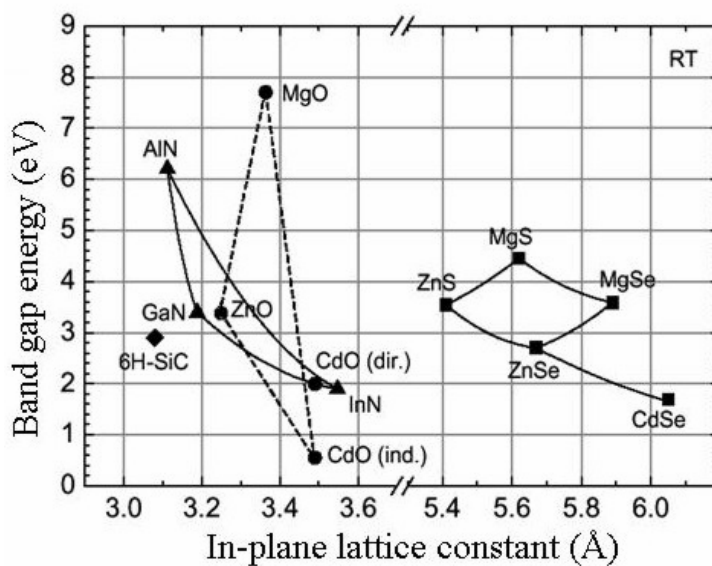


Figure 2.2: Wide band gap semiconductors; possibilities for band-gap engineering

refractive index, etc. and even its magnetic property for specific applications. Figure 2.2

shows the relationship between the in-plane lattice constant and the band gap energy for the family of wide band-gap semiconductors. For the ZnO material system, Cd and Mg all having two valence electrons can substitute Zn to decrease or increase the band gap of ZnO, respectively. As the broken line shows, band gap engineering in ZnO can be done within a wider energy range with reduced lattice misfit than in GaN. However, the hexagonal wurtzite structure of ZnO can be maintained only up to a certain Mg content, beyond which a change of phase occurs from wurtzite to rocksalt. There are controversial reports about the limit of Mg content in ZnMgO, within which the wurtzite structure is maintained. The maximum reported value for Mg content so far is 33% [MAK01].

ZnO has a great potential as the basis of diluted magnetic semiconductor (DMS) in the field of spintronics where ferromagnetic semiconductors are needed. By incorporating transition metals (TM) like Mn, V, Co, etc. in ZnO, ferromagnetic ZnTMO could be obtained. Such a semiconductor material could serve as channel for spin transport in the proposed spin transistor [DAT90] and for the realisation of the giant magnetic resistance (GMR) and tunnel magnetic resistance (TMR) phenomena for applications in devices like magnetic random access memory (MRAM), magnetic switch etc. In light-emitting structures, they would help in the realisation of circular polarised light [AND98]. There are some reports about ferromagnetism in transition metal-doped ZnO layers and nanostructures, for example, [JUN02] and [NOR03]. Even though these reports need verification, the introduced transition metals could additionally serve for band gap engineering.

2.2 Substrates for ZnO growth

The use of suitable substrate is an important aspect in the growth of semiconductors. The obvious approach is homoepitaxy, in which case one employs a substrate whose lattice parameters, crystal structure and thermal expansion coefficient are the same with those of the material to be grown, i.e. material to be grown and substrate are the same. One speaks of heteroepitaxy when the substrate material and the material to be grown are different. In the absence of homoepitaxial substrates, a substrate whose properties are very near to those of the desired semiconductor material can be used. Heteroepitaxy can also be preferentially done to exploit certain advantages, for example, the growth of InP or GaAs on silicon for monolithic integration of III-V optoelectronics and Si microelectronics [BAK03,MET89]. In the case of heteroepitaxy, several different epitaxy techniques can be employed to accommodate for lattice mismatch between the substrate and the semiconductor material to be grown, and thus minimise dislocation density. This is obvious during the growth of semiconductor layers. For

nanostructures, especially nanorods, heteroepitaxial substrates are not expected to lead to high dislocation density since the contact surface between the nanostructures and the substrate is small. In some sense, it could easily lead to the formation of nanostructures.

2.2.1 Commonly used substrates

ZnO substrates should be ideal for the growth of ZnO, however, there is general scarcity of such substrates and if available, they are very expensive. State-of-the-art quality ZnO substrates are produced through hydrothermal synthesis by a Japanese company, Tokyo Denpa and Eagle Picher in USA. Another supplier of ZnO substrates is CrysTec in Germany. All these substrates are still characterised by high dislocation density. It has rather been reported that homoepitaxy on ZnO substrates has proven to be more difficult than expected [GRA07]. Popular amongst heteroepitaxial substrates are Al_2O_3 , SiC, GaN and ScMgAlO_4 .

Table 2.2: *Some popular substrates used for the growth of ZnO*

	ZnO	Al_2O_3	GaN	6H-SiC	ScMgAlO_4	
a (nm)	0.325	0.4758	0.3189	0.308	0.3240	
c (nm)	0.569	1.299	0.5185	1.512	2.511	
Symmetry	W	H	W	W	T	
Linear expansion coefficient ($\times 10^{-6} \text{ K}^{-1}$)	a	8.25	7.5	5.59	4.2	6.2
	b	4.75	8.5	3.17	4.68	12.2

Table 2.2 shows the properties of some substrates used for the growth of ZnO. ScMgAlO_4 (commonly called SCAM) is the first substrate, on which ZnO-based light-emitting diodes were realised [TSU05]. It is tetragonal with its a lattice parameter almost equal to that of ZnO. However, the unavailability of this substrate makes it less promising for commercial ZnO growth. GaN has been used mostly in the form of epitaxial layers on Si or Al_2O_3 . Such quasi-substrates are not expected to lead to high quality ZnO crystals because the GaN epitaxial layers are characterised by high dislocation densities. These dislocations, as usual will thread into newly grown ZnO crystals. Besides the reported diffusion of Al into ZnO layers grown on Al_2O_3 substrates, they have so far proven to be the most suitable heteroepitaxial substrate, despite a large lattice mismatch of $\sim 19\%$ on the c -plane. Its hexagonal symmetry provides a good prerequisite for accommodating lattice mismatch for further growth of ZnO. Very narrow x-ray diffractometry *rocking curves* have been reported for ZnO layers (27 arcsec) [ELS06] and nanorods (750 arcsec) [MOF06] on (0001) and (11-20) Al_2O_3 substrates respectively. SiC also has the wurtzite structure, but with an a -axis lattice mismatch of $\sim 4\%$ to