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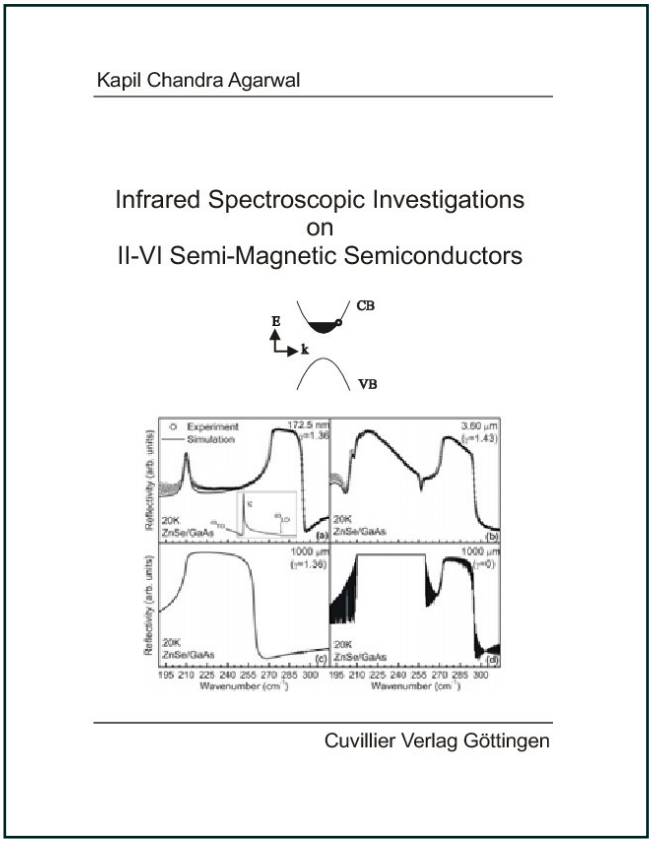
Infrared Spectroscopic Investigations on II-VI Semi-Magnetic Semiconductors

(with 53 Figures)



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Chapter 1

Introduction

1.1 Technological Interests

Integrated circuit (IC) and memory-storage technology are two of the most successful technologies used by industry today. Both are continuously growing at very rapid pace. Multinary semiconductor compounds allow 'tailoring' of the alloy's electronic and optical properties by varying the chemical composition of the alloy in order to have a precise match with the technological requirements for specific electronic and optoelectronic devices. However, conventional integrated circuits use only the charge property of the carriers (electrons/holes) and hence operate by controlling the flow of carriers through the semiconductor by applied electric fields. The characteristics of ICs include high speed signal processing and excellent reliability, but the memory elements are volatile (the stored information is lost when the power is switched off, as data is stored as charge in capacitors, i.e. DRAMs). However, in case of magnetic data storage, the key parameter is the spin of the electron, as spin can be thought of as the fundamental origin of magnetic moment. It is then quite natural to ask if we can utilize both, the charge and the spin property of electrons simultaneously, since this would lead to novel devices with enhanced performance. A successful example of this approach lies in "metal-spintronics" –a spin-valve.

The presently existing semiconductor devices utilize the charge of electrons and holes in order to perform their specific functionality such as signal processing or light emission. However, recently, there is a strong interest in the scientific community for realizing "semiconductor-spintronic" devices, which seek, in addition, to exploit the spin of charge carriers in a new generations of transistors, lasers and integrated magnetic sensors. The ability to control the spin injection, accumulation, transport and detection in

semiconductors leads to a potential for making novel photonic, logical, memory devices or even devices for quantum computing. Such devices are believed to be smaller, robust, ultra-low power and more versatile than those are currently in the use.

The fabrication of such devices depends on the availability of materials that can be utilized, e.g. as a spin-aligner for spin-injection. There are a number of semiconductor materials which attracted the attention of the scientific community for this purpose. Due to the giant Zeeman splitting at low temperatures, $Zn_{1-x}Mn_xSe$, a DMS (diluted magnetic semiconductor) is found as one of the promising candidates for aligning spins of the electrons [15]. In our group we try to combine a $Zn_{1-x}Mn_xSe$ spin aligner layer with a GaIn(N)As/GaAs quantum well/dot structures to realize spin-based optoelectronic devices. The physics behind spin-injection, transport and detection in the semiconductors should also be known for realization of such devices. Therefore, $Zn_{1-x}Mn_xSe$ can be used as spin-aligner either for designing a possible spin filter [10] or for investigation of spin-related phenomena in semiconductors. There is already a report by Jonker *et. al.* [16] about realization of 50% spin injection efficiency using $Zn_{0.94}Mn_{0.06}Se$ as a spin injecting contact on a GaAs-based light emitting diode.

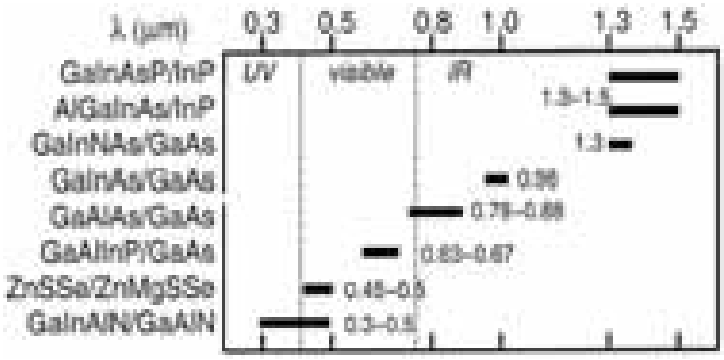

Figure 1.1: The emission wavelengths of different material systems in a wide spectral range [56].

In additional to spin-based optoelectronic devices, ZnSe-based materials are also interesting for other photonic devices. Figure 1.1 compares ZnSe-based materials with III-V direct band-gap semiconductors with respect to their emission wavelength range. ZnSe is a wide band-gap material, which has an advantage of being closely lattice matched to GaAs. This makes it possible to combine ZnSe-based semiconductor epilayers with III-V structures. ZnSe-based materials can be used to fabricate various optoelectronics devices, e.g. visible light-emitting diodes and blue-green laser diodes [1-7], electro-optic waveguide modulators for the blue-green spectral range [8], and blue-ultra violet photodetectors [9]. ZnSe is also a promising material as a barrier layer in magnetic tunnel junction (MTJ) based spin-LEDs [68].

1.2 OUR WORK

In the past decades, some studies on ZnSe-based materials have already been done. However, its semi-magnetic alloy $Zn_{1-x}Mn_xSe$ still holds some issues that are still unexplored and need to be investigated. For the full utilization of these materials either in spin-based optoelectronic devices or for making laser diodes, it is vitally important to have a solid knowledge about the fundamental material properties like bandgap, Γ_6-conduction band-edge mass, conduction band dispersion, doping possibilities and how these properties are influenced by incorporation of Mn into (Zn, Mn)Se bulk/quantum well structures. The vibrational spectra of $Zn_{1-x}Mn_xSe$ mixed crystal alloys are also of special interest in view of the fundamental aspects of lattice vibrations.

To our knowledge, there are no reports available in the literature for the electron effective mass in $Zn_{1-x}Mn_xSe$ [25]. Previous reports on long wavelength optical phonons in bulk and thin film $Zn_{1-x}Mn_xSe$ epilayers investigated via Raman scattering [20–22] and/or using far-infrared reflection and transmission studies [23, 24] provided some information about vibrational modes in $Zn_{1-x}Mn_xSe$ for a limited range of manganese contents. However, there was only experimental evidence for ZnSe-like and MnSe-like phonon features.

In the present work, unpolarized reflection measurements in the far-infrared to the mid-infrared spectral range are employed in combination with electrical Hall effect measurements to investigate the phonon and free-charge-carrier properties of $Zn_{1-x}Mn_xSe$ as a function of Mn content and free-electron concentration. Additionally, magneto-optic generalized ellipsometric (MOGE) measurements were carried out in collaboration with workgroup of Prof. Dr. M. Schubert at University of Leipzig, Germany.

Chapter 2 provides details about the crystal structure, the lattice constant and the band structure parameters of Zn(Mn)Se. The effect of manganese in $Zn_{1-x}Mn_xSe$ is reviewed in Sec. 2.6. In chapter 3, we discuss the various experimental techniques that were used in this work to investigate the Zn(Mn)Se/GaAs samples. Fourier transform infrared spectroscopy is the main experimental technique used in this work. A large section of this chapter is devoted to explain various steps used in FTIR data processing. Hall effect measurements and ellipsometry are also described briefly.

In chapter 4, we provide details about the growth and structure of the samples investigated in this work. Details about thickness and Mn content determination are given in Sec. 4.4 and 4.5, respectively. For a precise measurement of the free-electron

concentration, we prepared our samples in cloverleaf geometry using optical lithography. Details about the different steps used in sample preparation are provided in Sec. 4.6. In Sec. 4.7, we list all samples investigated in this work.

In chapter 5, we report the effect of Mn on the free-charge-carrier effective mass, free-electron concentration, mobility and resistivity in differently doped $Zn_{1-x}Mn_xSe$ samples. The electron effective mass extracted from plasma-edge and MOGE measurements are presented and discussed. The experimental electron effective mass values are compared with the theoretical ones. In chapter 6, we report and discuss our results about phonon properties in $Zn_{1-x}Mn_xSe$/GaAs samples containing up to very high Mn concentrations. The theoretical approach to fit the far-infrared reflection spectra of $Zn_{1-x}Mn_xSe$ *mixed alloys* is presented and discussed. The thickness effect on the shape of the reststrahlen band is explained in Sec. 6.7, based on experimental data and theoretical modeling. In chapter 7, we present a brief summary of our main findings obtained in this work. The bibliography contains all references used in this dissertation.

Chapter 2

Diluted magnetic semiconductor - (Zn, Mn)Se

2.1 INTRODUCTION

Zn(Mn)Se belongs to the family of II-VI diluted magnetic semiconductors (DMS). Sec. 2.2 starts with a basic introduction to the different DMS families. In Sec. 2.3, the discussion is focused especially on $Zn_{1-x}Mn_xSe$ semimagnetic semiconductor material. The precise knowledge of the crystal structure and lattice parameter is of fundamental importance. Therefore, in Sec. 2.4 we discuss the crystal structure and the lattice parameter of $Zn_{1-x}Mn_xSe$. The knowledge of the lattice parameter can also be used to determine the Mn content in the sample.

The electronic and optical properties of semiconductors are determined by their crystal and band structure. The band gap E_g determines the emission wavelength of the optical devices, e.g. light emitting diodes. In Sec. 2.5 we discuss important details about the band structure of ZnSe. The presence of Mn in $Zn_{1-x}Mn_xSe$ leads to new and interesting electrical and optical properties in this material. The band structure is also altered. In Sec. 2.6, we briefly discuss some of the important phenomena and/or the band structure modifications that arise due to the Mn incorporation in ZnSe-based semiconductors and alter their optical properties.

The giant Zeeman splitting of band-edges make this material interesting for semiconductor spintronic devices. In Sec. 2.7, we discuss various applications of ZnSe-based materials in different devices. However, due to the strong interest of the scientific community in spintronic devices, special attention is paid to describe its use as a spin-aligner in spin-based optoelectronic devices.

2.2 DILUTED MAGNETIC SEMICONDUCTORS

Diluted magnetic semiconductors (DMS) – sometimes also called semi-magnetic materials are semiconducting alloys whose lattice is made up in part of substitutional transition metal ions (such as Fe, Co, Ni, Mn or Cr) [11, 12]. The *dilute* incorporation of such magnetic ions (i.e., ions bearing a net magnetic moment) in a non-magnetic semiconductor can make them a member of the diluted magnetic semiconductors (DMS) family (Fig. 2.1).

Figure 2.1: A nonmagnetic polar semiconductor (left) can be converted to a DMS (right) after diluted incorporation of magnetic ions (i.e., ions bearing a net magnetic moment) in the host lattice.

The resulting DMS can behave as paramagnet or ferromagnet which varies for different host materials and different substitutional magnetic ions. There are different families of diluted magnetic semiconductors, for example II-VI DMS, III-V DMS or even IV-VI DMS. (Ga, Mn)As (T_C = 110 K) and (Ga, Mn)N (T_C = RT) are two examples of the family of III-V diluted magnetic semiconductors, which are ferromagnetic below their respective Curie temperature T_C [69]. The $Zn_{1-x}Mn_xO$ and $Zn_{1-x}Mn_xSe$ are two of the examples for the II-VI DMS family. In this work we are dealing with $Zn_{1-x}Mn_xSe$, a member of the II-VI DMS family. Therefore, in the following sections our discussion will remain focused mostly on the optical and electrical properties of the II-VI DMS.

2.3 ZnSe-Based DMS

In this dissertation, we focus on ZnSe-based DMS materials. $Zn_{1-x}Mn_xSe$ is a member of the $A^{II}_{1-x}Mn_xB^{VI}$ DMS family, in which a fraction of the group-II constituents (Zn^{2+} cations) are replaced by Mn^{2+} ions. There are good reasons behind the choice of Mn

in II-VI compounds—(i) Mn^{2+} can be incorporated in a sizeable amount into the $A^{II}B^{VI}$ host without affecting substantially the crystallographic quality of the resulting material (e.g., up to nearly 70% of Mn can be accommodated in ZnSe. (ii) Mn^{2+} possesses a relatively large magnetic moment (S = 5/2), characteristic of a half-filled *d*-shell (iii) Mn^{2+} is electrically neutral in $A^{II}B^{VI}$ hosts, i.e., it acts neither as an acceptor nor as an donator. So alloying Mn with II-VI semiconductors does not cause them to become *n*-type or *p*-type [55]. (It should be noted that in most III-V semiconductors, the Mn ions provide localized spins and act as acceptors, hence cause them to become *p*-type [69]).

The $Zn_{1-x}Mn_xSe$ ternary alloy (or "mixed crystal") is of interest for device applications and also from a research point of view due to several reasons. Firstly, the ternary nature of $A^{II}_{1-x}Mn_xB^{VI}$ DMS provides the possibility of "tuning" the lattice constant and band-gap by varying the concentration of Mn in the alloy. The relationship between the lattice constant and band gap energy in some important II-VI and III–V alloy semiconductors (including $Zn_{1-x}Mn_xSe$) is shown in Figure 2.2:

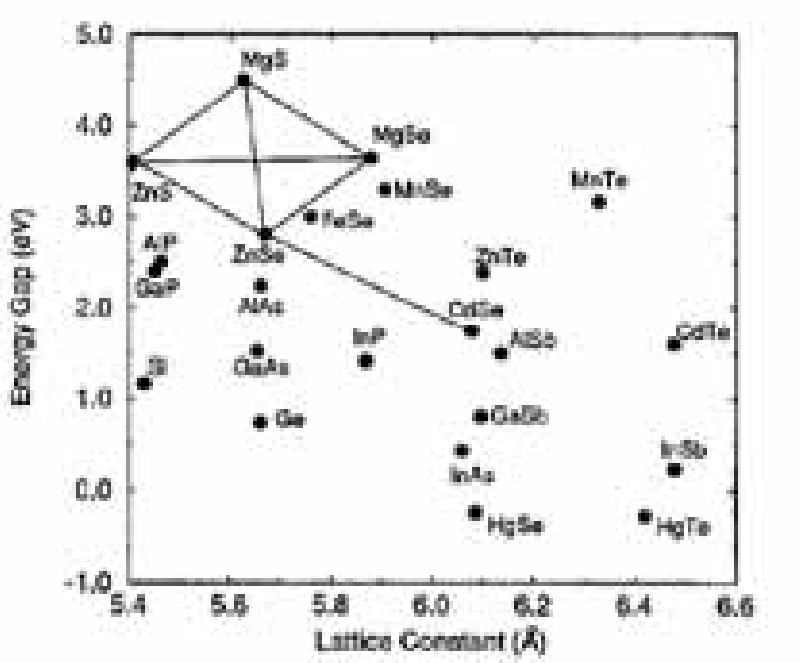

Figure 2.2: Relationship between the lattice constant and band gap energy in some important II-VI and III–V alloy semiconductors. Points show the binary compound semiconductors and curves show their ternary alloys [3].

Secondly, the large band gap and the close matching of the ZnSe lattice constant to that of GaAs make ZnSe-based materials interesting for a variety of potential applications in optoelectronic devices, e.g. light-emitting diodes and blue-green laser diodes [1-7], electro-optic waveguide modulators [8], as well as blue-ultraviolet photodetectors [9]. Thirdly, the random distribution of magnetic ions over the cation sublattice leads to interesting magnetic effects such as a spin-glass transition at low temperatures [12].

More importantly, the strong spin-spin exchange interaction between the electrons of the localized magnetic ions and the delocalized conduction band and/or valence band electrons causes the band-structure of the DMS material to be hundreds of times more sensitive to the strength of an external magnetic field than in ordinary semiconductors. The exchange interaction leads to a series of dramatic magneto-optical effects such as a huge Faraday rotation [55], giant Zeeman splitting of the band edges [11, 12, 14], and a magnetically tunable band gap [12]. The latter makes it a suitable candidate for the realization of spin-filters [10] or spin aligners in spin-based opto-electronic devices (see e.g. Refs. [15–18]). The highly efficient electroluminescence in $Zn_{1-x}Mn_xSe$ alloy also made it of considerable interest in the context of flat panel display devices [12].

2.4 CRYSTAL STRUCTURE AND LATTICE PARAMETER

The entire family of ternary $A^{II}_{1-x}Mn_xB^{VI}$ alloys, along with their crystal structure is presented in schematic form in Fig. 2.3. The bold lines in the figure show the composition ranges in which ternary alloys can be formed, with “cub” and “hex” indicating the crystal structure (zinc-blende and wurtzite, respectively) of the stable phases. For example, the alloy $Zn_{1-x}Mn_xSe$ exhibits zinc-blende structure for $x < 0.30$ and wurtzite structure for $0.30 < x < 0.55$ [38]. The values of x beyond the bold lines indicate the presence of mixed phases. Keeping in mind the fact that the stable structure of MnTe, MnSe and MnS differs from the crystal structure of the host material, it is truly remarkable that the range of the $A^{II}_{1-x}Mn_xB^{VI}$ solid solutions is so wide.

The atomic structures of Zn, Mn and Se atoms are as follows:

Zn (30): 2,8,18,2 $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\mathbf{3d^{10}}\,\mathbf{4s^2}$ **Group II**

Se (34) : 2,8,18,6 $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\mathbf{3d^{10}}\,\mathbf{4s^2}\,\mathbf{4p^4}$ **Group VI**