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Tesis Doctoral

Infrared intersubband detection and plasmonics with (Zn,Mg)O and (Cd,Zn)O compounds

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Abstract

English version

The aim of this thesis is to analyze ZnO- and CdO-based compounds and heterostructures to evaluate their prospects to develop emitting and detecting devices operating from the mid-infrared to the terahertz range of the electromagnetic spectrum. The dissertation encloses different studies divided into two main parts: ZnO-based compounds and heterostructures for intersubband detection and CdO-based compounds for mid-infrared plasmonics.

First, in order to understand the physical properties of ZnO, its alloy with MgO in wurtzite phase, and the effect of n-type doping with Ga, non-polar (Zn,Mg)O:Ga films are optically and electrically characterized.

The results show an increment of the bandgap of the alloy prior to phase segregation up to 4.41 eV, for a Mg content of 50 %. Also, the increase of the Mg content produced a clear compensation of free electrons. Nonetheless, an electron concentration of $4.4 \times 10^{19} \text{ cm}^{-3}$ was achieved in the alloy with 35 % Mg and a nominal Ga doping level of $4 \times 10^{19} \text{ cm}^{-3}$, implying a doping efficiency close to 100 %.

The knowledge acquired with the study of the (Zn,Mg)O:Ga alloys was used to design, grow and characterize ZnO:Ga/(Zn,Mg)O multiple quantum well heterostructures, with the aim of developing devices based on intersubband transitions: quantum well infrared photodetectors and quantum cascade lasers. The dependence of the frequency of the intersubband transitions on the quantum well thickness and the Ga doping level was analyzed, and the modeled absorption spectra agreed with the results. Quantum well thicknesses from 2.2 to 4.0 nm were probed: narrower quantum wells resulted in more energetic transitions, due to the larger separation of the energy levels within the quantum well. In wide quantum wells ($\geq 3.5 \text{ nm}$), three confined levels were theoretically predicted, and the dipole-dipole interaction of the two allowed intersubband transitions yielded the multisubband plasmon, a single effective intersubband transition resulting from the coupling of the individual oscillators. The theoretical predictions agreed with the experiments since a single absorption peak was observed at the frequency of the predicted multisubband plasmon. Besides, Ga doping produced a large blue-shift of the frequency of the multisubband plasmons, due to the depolarization effect.

The second part of the thesis covers the characterization of the (Cd,Zn)O alloy in rock-salt phase and the surface polaritons formed at its interfaces with the adjacent media.

The electrical characterization of the alloys shows a rise of the electron concentration with the Zn content, up to a value of $3.9 \times 10^{20} \text{ cm}^{-3}$. Besides, the measured electron mobility for Zn contents of 5, 10 and 15 % was determined to be higher with respect to that of CdO, with a maximum value of $110 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for 10 % Zn. The combination of the transport parameters of the alloy yielded resistivity values in the order of $10^{-4} \Omega \text{ cm}$, the lowest reported for the (Cd,Zn)O alloy and comparable with the values of common transparent conductive oxides. The results highlight the perspectives of this alloy for mid-infrared applications where efficient plasmonic materials with reduced optical losses are needed.

Once the Zn content (10 %) for which the alloy had the lowest optical losses was determined, the surface phenomena arising at its interfaces were studied. For doing so, (Cd,Zn)O alloys with different thicknesses were analyzed by means of attenuated total reflectance spectroscopy.

The focus was on the hybrid mode formed at the (Cd,Zn)O-sapphire interface: the surface plasmon (provided by the (Cd,Zn)O plasmonic material) was hybridized with the surface phonon (provided by the sapphire polar dielectric) to form the surface plasmon-phonon polariton. Its nature was observed to be modulable thanks to the control of the coupling strength of the fields at both interfaces, i.e. thanks to the accurate control of the alloy thickness. In thicker alloys ($\geq 150 \text{ nm}$) the frequencies of the hybrid mode were far from the reststrahlen band formed by the sapphire phonons, and therefore the mode acquired a plasmon-like behavior. Conversely, for lower (Cd,Zn)O thicknesses the frequencies of the hybrid mode approached those of sapphire phonons. Precisely at these frequencies a large enhancement of the propagation length of the mode along the interface was predicted, with a propagation distance larger than $500 \mu\text{m}$, one order of magnitude larger than that of typical surface plasmon polaritons. The enhancement of the propagation length improves the characteristics of the material for being employed in photonic devices where large propagation distances are required, such as plasmonic waveguides.

Versión española

La presente tesis doctoral analiza las características de heteroestructuras basadas en ZnO y CdO, con el objetivo de evaluar sus capacidades para el desarrollo de dispositivos detectores y emisores de luz en los rangos del infrarrojo medio y de los terahercios del espectro electromagnético. La tesis comprende distintos estudios, englobados en dos partes principales: compuestos basados en ZnO y heteroestructuras para la detección de transiciones intersubbanda y compuestos basados en CdO para su aplicación en plasmónica en el infrarrojo medio.

En primer lugar, con el objetivo de entender las propiedades físicas del ZnO, de su aleación con MgO en fase wurtzita, y de su dopaje tipo-n con Ga, se han caracterizado óptica y eléctricamente epicalas no polares de (Zn,Mg)O:Ga.

Los resultados prueban un incremento del *bandgap* de la aleación hasta los 4.41 eV para un contenido de Mg del 50 %. Además, el aumento del contenido de Mg produjo un efecto de compensación de electrones libres. Aun así, se llegó a alcanzar una concentración de electrones de $4.4 \times 10^{19} \text{ cm}^{-3}$ en la aleación con un 35 % de Mg y un dopaje nominal de Ga de $4 \times 10^{19} \text{ cm}^{-3}$, lo cual implica una eficiencia del dopaje cercana al 100 %.

El conocimiento adquirido con el estudio de las propiedades físicas de las aleaciones de (Zn,Mg)O:Ga se utilizó para el diseño, crecimiento y caracterización de las estructuras de multipozos cuánticos de ZnO:Ga/(Zn,Mg)O, con el objetivo de la detección de transiciones de intersubbanda, como primer paso para el desarrollo de fotodetectores de infrarrojo de pozos cuánticos y láseres de cascada cuántica. La dependencia de la frecuencia de las transiciones intersubbanda tanto con el espesor de los pozos cuánticos de ZnO:Ga como con su nivel de dopaje de Ga fue analizada, y los resultados fueron corroborados con espectros de absorción modelados computacionalmente. Pozos cuánticos con espesores desde 2.2 hasta 4.0 nm fueron caracterizados: los pozos cuánticos más estrechos dieron lugar a transiciones más energéticas, debido a la mayor separación energética entre los niveles del pozo cuántico. Además, en pozos cuánticos anchos (≥ 3.5 nm) los modelos predijeron la formación de tres niveles confinados, y la interacción entre los dipolos de las dos transiciones intersubbanda permitidas dio lugar al plasmón multisubbanda, una única transición resultante del acoplo de los dos osciladores individuales. Los experimentos confirmaron los modelos teóricos, ya que se observó un

único pico de absorción a la frecuencia predicha para el plasmón de multisubbanda. Además, los dopajes de Ga produjeron un desplazamiento del pico de absorción hacia mayores energías, debido al efecto de depolarización.

El segundo bloque de la tesis aborda la caracterización de la aleación de (Cd,Zn)O en fase *rock-salt* y los polaritones de superficie formados en sus intercaras con el medio adyacente.

La caracterización eléctrica de las aleaciones mostró un aumento de la concentración de electrones libres con el contenido de Zn, llegando hasta un máximo de $3.9 \times 10^{20} \text{ cm}^{-3}$. Además, la movilidad de los electrones para contenidos de Zn de 5, 10 y 15 % resultó ser mayor que la obtenida para el binario CdO, con un valor máximo de $110 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ para un contenido de Zn del 10 %. Combinando los parámetros de transporte se calculó la resistividad de las aleaciones, encontrándose en el orden de magnitud de $10^{-4} \Omega \text{ cm}$. Los valores obtenidos corresponden a las menores resistividades publicadas para la aleación de (Cd,Zn)O, siendo además comparables a las resistividades de los materiales comúnmente utilizados como óxidos conductores transparentes. Los resultados suponen una mejora de las perspectivas de la aleación para aplicaciones en el infrarrojo medio, donde son necesarios materiales plasmónicos con bajas pérdidas.

La aleación de (Cd,Zn)O con un contenido de Zn del 10 % mostró las menores pérdidas y fue empleada para estudiar los fenómenos de superficie formados en sus intercaras. Para ello, aleaciones con distintos espesores fueron analizadas por medio de la técnica de reflexión total atenuada.

El estudio se centró en el modo híbrido formado en la intercara (Cd,Zn)O-zafiro: el plasmón de superficie del (Cd,Zn)O se hibridó con el fonón de superficie del zafiro, para dar lugar al polaritón de superficie plasmón-fonón. Se observó que la naturaleza del mismo podía ser modulable gracias al control sobre el acoplo de los campos entre las dos intercaras de la aleación, esto es, gracias al preciso control del espesor de la aleación. Para aleaciones más gruesas ($\geq 150 \text{ nm}$), las frecuencias del modo híbrido fueron mucho más energéticas que las de la *reststrahlen band* formada por los fonones del zafiro, y por lo tanto el modo presentaba un comportamiento plasmónico. Por el contrario, para menores espesores las frecuencias del modo híbrido se aproximaban a las de los fonones del zafiro. Precisamente para esas frecuencias se predijo teóricamente una gran mejora de la distancia de propagación a lo largo de la intercara, alcanzando valores superiores a $500 \mu\text{m}$, un orden

de magnitud mayor que las distancias de propagación típicamente obtenidas en modos de superficie puramente plasmónicos. Esta mejora de la distancia de propagación, una de las principales características de los modos de superficie, supone un gran avance para la implementación de este modo híbrido en dispositivos fotónicos en los que se requieren largas distancias de propagación, como por ejemplo en guías de onda plasmónicas.

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Part I

Introduction, theory, and characterization techniques

Chapter 1. Introduction

1.1. State of the art and motivation

In the last century, there was a great revolution in the field of electronics, assisted by the rapidly acquired knowledge of semiconductor physics and engineering and the emergence of new and most reliable manufacturing techniques. The first advances of semiconductor physics took place in the 19th century. In 1833 the first semiconductor effect was recorded by Faraday, who observed the conductivity of Ag_2S increased with temperature.¹ A few years later, in 1839, Becquerel reported the first observation of the photovoltaic effect in a junction between a semiconductor and an electrolyte.² In 1909, Braun, together with Marconi, won the Nobel Prize in physics for their contribution to the development of wireless communication. The basis of this prize was seeded by Braun in 1874 with the observation of rectification in metal sulfides.³

The research done in this field in the following decades led to the fabrication of the first semiconductor devices. During the first decades of the 20th century, the point-contact rectifiers were improved, from the original one of PbS patented by Bose in 1904.⁴ Among all the semiconductor devices developed, the bipolar transistor set a turning point that has lasted to this day, with most of the daily used electronic devices containing thousands of transistors. In 1947, Bardeen and Brattain built the first point-contact transistor⁵ and Shockley formulated the theory of the p-n junction,⁶ thanks to what they won the Nobel Prize in physics in 1956 for their discovery of the transistor effect.

Up to now, Si is the most extended semiconductor in the industry of electronics, being the base of the CMOS technology for manufacturing integrated circuits. However, the increasing demand to develop devices with improved characteristics and the discovery of new physical properties in alternative semiconductors widened the spectrum of semiconductor compounds, included III-V semiconductors. InSb was the first III-V semiconductor discovered, in 1950, with the narrowest bandgap semiconductor at that time (0.18 eV), and it has been studied for far-infrared (far-IR) detection technology.⁷ The regimes of ultraviolet (UV) and visible (VIS) are mainly governed by the GaN binary, with a wider bandgap of 3.39 eV.⁸ The first GaN-based light emitting device (LED) was reported in 1971 by Pankove *et al.*⁹ and nowadays blue and green nitride-based LEDs are used in a variety of displays. Another popular III-V semiconductor is GaAs, with which the first laser diode device was made in 1962, emitting at 850 nm.¹⁰ Besides, compared to Si and Ge,

GaAs has a very high electron mobility so it has been popularized for manufacturing high-speed electronic devices. In III-V compounds, the elements from the group III are transferring charge to that of the group V, so the bonding starts to acquire an ionic character. The ionicity of the system is larger for II-VI compounds, altering the electronic properties of the material to a greater extent. For instance, the ionicity tends to increase the bandgap of the compound so in general II-VI semiconductors have a wider bandgap than III-V semiconductors, making them potential candidates for VIS-UV applications. To this group of semiconductors belong ZnO and CdO, which the doctoral thesis will cover.

The high chemical stability, biocompatibility and low manufacturing cost of ZnO¹¹ and its bandgap (3.37 eV¹²) between the UV and VIS regions of the electromagnetic spectrum make it a promising semiconductor to cover the UV-VIS range. The first time a photoresponse was observed in ZnO films was in the 1940s by Mollow,¹³ and the photoconductive properties of ZnO were further studied the following decades.^{14,15} The first Schottky barriers in ZnO-metal interfaces were demonstrated in 1965 by Mead, with metals such as Au and Cu.¹⁶ To overcome the difficulties of producing p-type ZnO, other materials were used to form p-n junctions. Thus, in 1967, the first LEDs in ZnO-based heterostructures were demonstrated by Drapak,¹⁷ where Cu₂O was used as the p-type contact. The advances made on the synthesis of ZnO thin films in recent years has enhanced the performance of complex ZnO-based photodetectors.¹⁸

The development of new growth techniques, such as molecular beam epitaxy (MBE), that allows to grow thin films epitaxially and with lower impurity and defect concentration, and the availability of high-quality ZnO substrates, has renewed the interest in ZnO. A good example is the integration of ZnO as a transparent conductive electrode,¹⁹ taking advantage of its wide bandgap and n-type character. Besides, ZnO can be alloyed with other oxides, as MgO and CdO, allowing to tune the optical and transport properties of the compound and spreading its range of applications.

As a result, a new demand has emerged for ZnO in the last years: the exploration of the mid-infrared (mid-IR) and terahertz (THz) regimes with ZnO:Ga/(Zn,Mg)O-based devices. The mid-IR, with wavelengths from ~ 2 to 30 μm , corresponds to the range where the thermal emission peak of bodies with temperatures between 200 to 1400 K falls, and therefore thermal imaging is a direct application. In addition, the rotational and vibrational excitations of many molecules have energies in the mid-IR, and therefore is the mid-IR a highly used region in spectroscopy and molecular sensing applications.

The sources in the mid-IR range of the electromagnetic spectrum use different laser technologies, each with advantages and drawbacks. In Figure 1.1, different available coherent sources in the near-IR and mid-IR are compared.

Figure 1.1. Laser sources and their wavelength coverage in the near-IR and mid-IR regions of the electromagnetic spectrum. Taken from reference 20.

One of the first available sources were lead-salt diode lasers, in which stimulated emission is produced between the conduction and valence bands.²⁰ However, they require a cryogenic cooling stage to operate and exhibit a low power performance. Nonlinear sources are also commonly used, where mid-IR radiation is achieved from the parametric frequency conversion of near-IR sources,²⁰ but the synthesis and processing of such complex systems is rather expensive.²¹

In this context, a relative new technology emerged: quantum cascade lasers (QCLs), based on intersubband transitions (ISBTs). While QCLs exhibit an excellent performance in the mid-IR, the possibility to tune the lasing frequency to the THz regime is a challengeable feature for this technology. Indeed, the THz range is also known as “the THz gap”, due to the lack of high power and low-cost semiconductor devices covering the THz region.²² Nowadays, the military and health industries, among others, are demanding new, less expensive and more compact THz laser sources and detectors. THz radiation has the advantage of being non-ionizing and having a deep penetration in organic materials. Besides, water molecules absorb in the THz, thus, it has applications for sensing and mapping biological tissues.^{23,24} THz radiation can also penetrate through some materials

such as plastic or paper with low attenuation, and therefore it can be used for imaging and detecting hidden explosives and weapons. In addition, THz radiation is utilized in astronomy, since many emitted photons have energies in the THz range.²⁵ Hence the importance of developing new sources and detectors for the THz range.

The first experimental demonstration of a QCL was in 1994 in the Bell laboratories by the group of Prof. Federico Capasso,²⁶ with an output power of 8 mW at 4.2 μm . The most extended heterostructures used for QCLs are based on GaAs, however, the main drawback of III-V semiconductors, is their very low working temperature. They exhibit an optimum performance in the mid-IR range, however, in the THz range the working temperature has to be maintained below 200 K because of non-radiative losses.²⁷ In theory, the constraint of the low working temperature can be overcome with ZnO-based devices, thanks to the more favorable intrinsic properties of the material (discussed in Section 2.4.5), and thus they are proposed for fabricating QCLs. In a complementary way, mid-IR and THz detection can be realized with quantum well infrared photodetectors (QWIPs), also based on ISBTs.

The other semiconductor studied in this thesis is CdO, an n-type semiconductor with excellent transport properties that has received great attention for its application as a transparent conducting oxide (TCO).²⁸ TCOs are characterized by their high conductivity as well as their wide transmission window. These characteristics are required for the electrodes of many devices such as LEDs, solar cells and flat panel displays.²⁸ Traditionally, indium tin oxide (ITO) has been the most used TCO, but the shortage of indium reserves in the world²⁸ makes it necessary to look for alternatives, and CdO is a good candidate, thanks to its high electron concentrations and high electron mobilities present in as-grown material.^{29,30} Indeed, the first TCO film ever reported consisted of a vacuum sputtered Cd metal film thermally oxidized to form CdO, synthesized in 1907 by Badeker.³¹ It was not until 1950 when the performance of a CdO electrode was studied in Se photovoltaic cells,³² showing a suitable barrier height formed between the Se/CdO interface and yielding a high sensitivity and photovoltage. Two decades later a CdO electrode was studied for silicon photodiodes,³³ with transmission values of 80 % for wavelengths above 500 nm. The interest of CdO as a TCO was maintained during the first years of the 21st century, with enhanced electrical conductivities observed when it is doped with other elements, such as F,³⁴ Al,³⁵ In,³⁶ Sn,³⁷ or Dy.³⁸

In recent years CdO has also been studied for its application as a low-loss plasmonic material in the mid-IR,³⁸ playing the same role than noble metals in the VIS and UV spectral

ranges. The high electron concentration ($\sim 10^{20} \text{ cm}^{-3}$) as well as the high optical mobility ($\sim 600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)³⁰ present in as-grown material, make CdO a promising material for mid-IR plasmonics with very low losses compared to other TCOs. Besides, the ability to tune the electron concentration and reduce the optical losses of CdO by alloying it with ZnO improves the perspectives of this TCO.

1.2. Goals and framework

In this thesis, the capabilities of 2D heterostructures based on ZnO and CdO and its alloys are addressed. Thus, two work lines are distinguished: ZnO:Ga/(Zn,Mg)O heterostructures for mid-IR intersubband applications and the (Cd,Zn)O alloy as conducting metal oxide and low-loss plasmonic material.

Concerning the ZnO-based heterostructures, the work is framed within the ZOTERAC Project (Zinc Oxide For TeraHertz Cascade Devices) of the European Union, starting at the same time as the thesis program, on September 2015, and finishing on September 2019.³⁹ The project is carried out together with other research institutions from the European Union: Assoc. Prof. Jean-Michel Chauveau, coordinator of the project, from *Centre National de la Recherche Scientifique* (CNRS, France), Prof. Gottfried Strasser from *Technische Universität Wien* (TUW, Austria), Dr. François Julien from *Université Paris Sud* (France), Prof. Jérôme Faist from *Eidgenössische Technische Hochschule Zürich* (ETH, Switzerland), and the institution where the thesis is done, *Instituto de Sistemas Optoelectrónicos y Microtecnología* ascribed to *Universidad Politécnica de Madrid* (ISOM-UPM, Spain). The ISB samples used in this thesis were thus grown by molecular beam epitaxy at CNRS by the group of Assoc. Prof. Jean-Michel Chauveau.

Regarding CdO and its alloy with ZnO, the work is framed on the national projects TEC2014-60173-C2-2 and TEC2017-85912-C2-1-R, funded by the Spanish Ministry of Economy and Competitiveness (MINECO). These projects are carried out with the collaboration of *Universitat de València* (Spain) where the (Cd,Zn)O alloys were grown by metal-organic chemical vapor deposition.

Thus, the objectives of the thesis are divided into two blocks:

ZnO-based heterostructures

- I. The study and understanding of the physical properties of the (Zn,Mg)O:Ga ternary in the wurtzite phase.

- II. The design of ZnO:Ga/(Zn,Mg)O heterostructures to be applied in mid-IR detectors.
- III. The demonstration of ISB absorption in ZnO:Ga/(Zn,Mg)O multiple quantum wells (MQWs).
- IV. The processing of QWIPs and the demonstration of ISB-based photocurrent.

(Cd,Zn)O alloys for mid-IR applications

- I. The study and understanding of the transport and optical properties of the (Cd,Zn)O ternary in rock-salt phase.
- II. The optimization of the alloy parameters for its application as a TCO and as a low-loss plasmonic material.
- III. The detection and study of the surface polaritons arising in the air-(Cd,Zn)O-sapphire system.

1.3. Structure of the thesis

The thesis is divided into four parts, each with the following chapters:

Part I. Introduction, theory, and characterization techniques.

Chapter 1. State of the art and motivation, goals and framework.

Chapter 2. Properties of ZnO and CdO and theoretical basis of the physical phenomena studied in each material.

Chapter 3. Characterization and processing techniques employed to analyze the optical and electrical properties of the oxides and mid-IR devices.

Part II. Results: ZnO:Ga/(Zn,Mg)O heterostructures.

Chapter 4. Electrical and optical characterization of the (Zn,Mg)O:Ga alloys and understanding the interplay between the Mg and Ga atoms in the crystalline structure of ZnO.

Chapter 5. Design of ZnO:Ga/(Zn,Mg)O multiple quantum wells, ISB detection and development of QWIPs.

Part III. Results: (Cd,Zn)O ternary.

Chapter 6. Electrical and optical properties of the (Cd,Zn)O alloy and optimization of the Zn content for its implementation as a TCO and low-loss plasmonic material.

Chapter 7. Analysis of the surface polaritons in (Cd,Zn)O alloys with different thicknesses and observation of the epsilon-near-zero mode.

Part IV. Conclusions and future work.

Chapter 8. Summary of the main conclusions derived from the results and perspectives for future studies and applications.

Chapter 2. Heterostructures based on ZnO and CdO

This chapter is devoted to introduce the physical properties of the oxides treated in the thesis and the theory on which the ISB and plasmonic phenomena are based. Note the objective of the author is not to describe the full theory behind these physical phenomena but to give a summary of the most important theoretical fundamentals on which the results described in chapters 5 and 7 are based.

The reader can find extended details about the theory of intersubband transitions in quantum wells in the books “Quantum Well Infrared Photodetectors”, by H. Schneider and H.C. Liu,⁴⁰ and “Intersubband Transitions in Quantum Wells: Physics and Device Applications I” by H. C. Liu and F. Capasso.⁴¹

Concerning the plasmonics phenomena, two excellent sources where a detailed discussion can be found are the books “Surface modes in physics”, by Bo E. Sernelius,⁴² and “Plasmonics: Fundamentals and Applications”, by S. A. Maier.⁴³

2.1. Properties of ZnO

ZnO is an n-type, II-VI semiconductor, with a room-temperature direct bandgap of 3.37 eV.¹² ZnO is found in three crystalline structures: wurtzite, zinc blende, and rock-salt. However, under ambient conditions ZnO crystallizes in the wurtzite hexagonal structure, represented in Figure 2.1, with lattice constants $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$.⁴⁴ In this structure, each cation Zn^{2+} is surrounded by four O^{2-} anions and *vice versa*, giving an ionic character to the material. The c -axis connects the hexagonal crystallographic planes, i.e. the c -planes, and, due to the ionicity, ZnO acquires a piezoelectric behavior, with a spontaneous polarization along the c -axis.

The anisotropy of ZnO also influences the vibrational properties of its lattice. Transversal optical (TO) and longitudinal optical (LO) phonons unfold into axial and planar modes, with the atoms vibrating parallel or perpendicular to the c -axis, respectively.⁴⁵ Both axial and planar modes are Raman and infrared active, with values of 378 cm^{-1} (TO) and 575 cm^{-1} (LO) for the axial phonons and 409 cm^{-1} (TO) and 590 cm^{-1} (LO) for the planar ones.

The exciton binding energy of ZnO (60 meV at room temperature) is much larger than that of other III-V semiconductors, such as GaN (23 meV), providing an optimum thermal stability for exciton-based optoelectronic devices.

Figure 2.1. Wurtzite structure of ZnO, with Zn atoms in green and O atoms in red. The lattice constants a and c as well as the m -, c -, r -, and a -planes are indicated.

Regarding the transport properties of ZnO, a key parameter is the electron effective mass (m_e^*), which is commonly accepted to be $0.24 m_0$ (where m_0 is the free electron mass).⁴⁶ Nevertheless, as a result of the ionicity of ZnO, electrons are highly coupled to lattice vibrations yielding a polaron, and thus m_e^* can be as high as $0.28 m_0$.⁴⁷

Nowadays, the availability of ZnO high quality substrates combined with the optimized growth by using different techniques can reduce the residual electron concentration of n-type ZnO to as low as 10^{14} cm^{-3} .⁴⁸ The source of the n-type conductivity is ascribed to the formation of intrinsic defects during the growth process. During many decades, it was attributed to the formation of oxygen vacancies, however, nowadays other sources as hydrogen-related impurities must be considered.⁴⁹

2.1.1. Doping ZnO with Ga and alloying with MgO in wurtzite phase

The optical and transport properties of ZnO can be modulated by doping and alloying it with other materials, widening the range of applications of the material. In particular, elements from Groups III and VII of the periodic table are potential agents as donors in ZnO. Hence, among others, Al,⁵⁰ Ga,⁵¹ or In⁵² have been studied as candidates for doping ZnO, and an electron concentration as large as $1 \times 10^{21} \text{ cm}^{-3}$ has been achieved in

ZnO:Ga.⁵³ Throughout the thesis, the dopant employed is Ga, with an atomic radius similar to that of Zn, and more robust to oxidation and less reactive than Al.⁵⁴

Figure 2.2. Bandgaps of ZnO, CdO, and MgO and their alloys vs their lattice constants. Hexagonal green symbols represent the wurtzite phase and purple square symbols the rock-salt phase. The stable phase of each compound is indicated in black.

When a higher ratio of substitutional atoms is added to ZnO the band structure is modified, and the material is considered an alloy rather than a doped material. ZnO can be alloyed with CdO and MgO, resulting in a narrower and larger bandgap than ZnO, respectively, as represented in Figure 2.2. Ideally, the bandgap of ZnO could be increased from 3.37 eV of pure ZnO to 6.4 eV of MgO,⁵⁵ while maintaining the wurtzite structure. Likewise, when ZnO is alloyed with CdO, the bandgap could be reduced to 0.92 eV,⁵⁵ also in the wurtzite structure. However, the thermodynamically-stable crystalline structure of MgO and CdO is rock-salt and, as a result, phase segregation is expected at some Mg or Cd content, in each case.

In this thesis, the analysis of the (Zn,Mg)O:Ga alloy in the wurtzite phase is covered, in order to determine its physical properties for the growth of optimized multiple quantum well heterostructures. The tetrahedral atomic radius of Mg^{2+} is 0.57 Å, similar to that of Zn^{2+} (0.60 Å), so the solubility limit of Mg in ZnO is expected to be high and to vary depending on the growth technique employed. For instance, prior to phase segregation, 36 % Mg has been successfully incorporated in films grown by pulsed laser deposition,⁵⁶

up to a maximum of 56 % for films grown by MBE.⁵⁷ The critical thickness before plastic relaxation occurs for a given Mg content and has to be considered when growing 2D heterostructures.⁵⁸

Thanks to the similar atomic radius of Zn^{2+} and Mg^{2+} , in $\text{ZnO:Ga}/(\text{Zn,Mg})\text{O}$ multiple QWs the strain due to the lattice mismatch between the $(\text{Zn,Mg})\text{O}$ ternary and the ZnO:Ga binary can be expected to be low. However, the replacement of Zn^{2+} atoms by Mg^{2+} has been proved to produce a shrinkage of the lattice along the c -axis and an expansion along the a -axis, with the cell volume remaining almost independent of the Mg content.⁵⁹

2.2. Properties of CdO

CdO is also a II-VI semiconductor, and under ambient conditions it crystallizes in the rock-salt phase, with both Cd and O atoms forming a face-centered cubic lattice, as shown in Figure 2.3.

Figure 2.3. Rock-salt structure of CdO, with Cd atoms in blue and O atoms in red.

The lattice constant is $a = 4.6942 \text{ \AA}$, and the Cd^{2+} atoms are coordinated to 6 O^{2-} atoms at the vertices of an octahedron (and *vice versa*).⁶⁰ The symmetry of the cubic structure reduces the number of phonon modes of the crystal. From infrared measurements, the frequencies of the TO and LO modes in the center of the Brillouin zone were determined to be 262 and 523 cm^{-1} , respectively.⁶¹ More recent *ab initio* calculations were performed,⁶² showing a great agreement for the TO frequency (262 cm^{-1}) but a large mismatch for the LO frequency (431 cm^{-1}).

CdO is an n-type semiconductor, with a high electron concentration present in as-grown, unintentionally doped material ($\sim 10^{20} \text{ cm}^{-3}$). The consequence is a large blue shift of the fundamental optical absorption edge, first observed in CdO in 1954 by Stuke,⁶³ the same year the Burstein's interpretation of the blue shift was made on InSb.⁶⁴ In rock-salt phase, CdO has an indirect bandgap of about 1 eV,⁶⁵ and a direct bandgap at the Γ point of 2.2 eV,³⁰ however, due to the Burstein-Moss shift, the absorption band-edge energy is around 2.5 eV.²⁹ Another phenomena to be considered in a degenerate semiconductor is the conduction band (CB) non-parabolicity, which affects the electron effective mass. In CdO, at the CB minimum, the effective mass is $0.21 m_0$, however, as the Fermi level shifts to higher energies, the effective mass increases.²⁹ Despite the high electron effective mass of CdO compared to other semiconductors, and the high electron concentration present in as-grown material ($\sim 10^{20} \text{ cm}^{-3}$), the transport mobility can also be large ($\sim 100 \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$),³⁰ yielding low resistivities ($\sim 10^{-4} \Omega \text{ cm}$).

In contrast to ZnO, O vacancies (V_o) have been considered the main source of electrons in CdO, acting as doubly ionized shallow donors. Besides, in recent years H impurities have gained attention for being potential donors in CdO.^{66–68}

2.2.1. Alloying CdO with ZnO in the rock-salt phase

The direct bandgap of CdO at the Γ point can be increased by alloying it with ZnO or MgO, with direct bandgaps in the rock-salt phase of 4.5 eV⁶⁹ and 7.9 eV,⁷⁰ respectively, as represented in Figure 2.2. However, the thermodynamically-stable crystalline structure of ZnO is wurtzite while that of CdO is rock-salt, and when the Zn content in the (Cd,Zn)O alloy is increased, the challenge of phase segregation arises. Therefore, the maximum Zn content attainable before phase segregation will be restricted.

The (Zn,Cd)O ternary in wurtzite phase, i.e. the ternary on which Cd atoms are introduced in the crystalline structure of ZnO, has been widely explored with different growth techniques, such as pulsed laser deposition,⁷¹ reactive direct-current magnetron sputtering,⁷² MBE,⁷³ the sol-gel method,⁷⁴ and metal-organic chemical vapor deposition (MOCVD)⁷⁵, and Cd is known to reduce the bandgap and to increase the free electron concentration of the material. However, the (Cd,Zn)O ternary in rock-salt phase, i.e. the ternary on which Zn atoms are introduced in the crystalline structure of CdO, remains almost unexplored, only for polycrystalline thin films grown by spray pyrolysis^{76–78} and sol-gel spin coating methods.^{79–81} Thanks to the very large electron concentration and

mobility present in as-grown CdO, the rock-salt (Cd,Zn)O alloy is expected to exhibit these characteristics or even improved transport properties for increasing Zn contents.

2.3. From bulk to thin films

The motion of electrons in solids is described by the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_0} \nabla^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}), \quad (2.1)$$

where m_0 is the free electron mass, $\Psi(\mathbf{r})$ is the wave function of the electron and $V(\mathbf{r})$ is the potential of the crystal. When electrons are free to move in any direction $V(\mathbf{r}) = 0$, and the solution of the Schrödinger equation gives a continuum of available energy values E , and a wave function $\Psi(\mathbf{r})$ in the form of a plane wave with wavevector $\mathbf{k}$, as

$$E = \frac{\hbar^2 \mathbf{k}^2}{2m_0}; \quad \Psi(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r}). \quad (2.2)$$

However, in crystals electrons “feel” a periodic potential $V(\mathbf{r})$, and the solutions of the Schrödinger equation are wavefunctions represented by the Bloch function

$$\Psi(\mathbf{r}) = u(\mathbf{r})\exp(i\mathbf{k}\mathbf{r}), \quad (2.3)$$

composed by $u(\mathbf{r})$, with the same periodicity as $V(\mathbf{r})$, and plane waves. The band structure of the material is given by the representation of the available energy levels vs $\mathbf{k}$. Bragg reflections at the boundaries of the Brillouin zone (i.e. at $k = \pm n\pi/a$ in a one-dimensional system with a lattice constant a) form the energy bandgaps, and their absolute values depend on the strength of the potential profile.⁸²

The electron density of states is defined as the number of solutions allowed by the Schrödinger equation per unit of volume and energy. When the length of the system approaches the Broglie wavelength of the particles on it (electrons in n-type semiconductors), the density of states is quantized, as shown in Figure 2.4.

In the ZnO:Ga/(Zn,Mg)O 2D systems analyzed in this thesis, the observed quantum phenomena described in Chapter 5 is intimately related to the 2D-quantization of the density of states. In particular, a 2D system will be formed in the CB of the heterostructures, with ZnO:Ga thin films forming the quantum wells and (Zn,Mg)O thin films being the barriers.

Figure 2.4. Density of states as a function of energy according to the system dimensionality.

2.4. Two dimensional ZnO:Ga/(Zn,Mg)O multiple quantum wells

2.4.1. Bandgap engineering

The CB offset formed in the junction of two semiconductors, as is the case of the ZnO:Ga/(Zn,Mg)O interface, is determined by the Anderson's rule,⁸³ which states the band alignment is given by the electron affinity of both materials. Thus, the heterojunction could be aligned in three different ways, as depicted in Figure 2.5.

Figure 2.5. Types of heterojunctions following Anderson's rule.

In the case of the ZnO:Ga/(Zn,Mg)O system, the CB to valence band (VB) offset ratio is in between 0.65/0.35 to 0.70/0.30, as reported elsewhere,^{84–86} and the heterojunction

is of type I. The direct bandgap of the (Zn,Mg)O alloy increases from the 3.37 eV of ZnO at a rate of 25 meV per % of Mg, as reported by Neumann *et al.*⁸⁷

The ZnO polarity has also to be considered when growing heterostructures: the spontaneous polarization along the c -axis may induce a CB bending of the multiple quantum wells when samples are grown in the polar c -plane orientation, i.e. with the c -axis perpendicular to the growth direction. The ZnO:Ga/(Zn,Mg)O samples analyzed in this thesis are grown in the m -plane non-polar orientation, in order to avoid undesired effects such as the quantum confined Stark effect,⁸⁸ which could have a detrimental impact on the performance of future devices.

2.4.2. Subbands in a quantum well

The oxides treated in this thesis have n-type conductivity, and therefore they are studied for their implementation in unipolar devices. The physical phenomena on which these devices are based takes place in the CB, thus, the following analysis is restricted to the CB of the ZnO:Ga/(Zn,Mg)O heterostructures, within the effective mass approximation. The system is schematized in Figure 2.6.

Figure 2.6. (a) Finite QW with two confined energy levels and (b) their in-plane energy subbands.

Setting the z -axis as the growth direction of the QWs and (x, y) the in-plane directions, the CB potential profile is defined as

$$V(x, y) = 0 \quad \forall x, y \quad (2.4.a)$$

$$V(z) = \begin{cases} 0 & -a/2 < z < a/2 \\ \Delta E_c & z < -a/2 \text{ \& } z > a/2, \end{cases} \quad (2.4.b)$$

where a is the thickness of the QW, and ΔE_c the CB offset. Thus, the wavefunction can be written as the product of an envelope function $\chi(\mathbf{r})$ and the Bloch function $\Psi(\mathbf{r})$, and the Schrödinger equation is rewritten as follows

$$\left[-\frac{\hbar^2}{2m^*(z)} \nabla^2 + V(z) \right] \chi(\mathbf{r}) \Psi(\mathbf{r}) = E \chi(\mathbf{r}) \Psi(\mathbf{r}), \quad (2.5)$$

with

$$m^*(z) \begin{cases} m_{(Zn,Mg)O}^* \equiv m_b & z < -a/2; z > a/2 \\ m_{ZnO}^* \equiv m_{QW} & -a/2 < z < a/2. \end{cases} \quad (2.6.a)$$

$$(2.6.b)$$

At the same time and due to the system anisotropy, the envelope function can be divided into the in-plane and out-of-plane components, each with its associated energy, i.e. $\chi(\mathbf{r}) = \varphi(x,y)\phi(z)$ with $E = E_{xy} + E_z$. Regarding the in-plane solutions, since the potential $V(x,y) = 0$, the Hamiltonian is reduced to the kinetic energy of the electrons and the in-plane wavefunction of the electron adopts the form of a plane wave

$$E(\mathbf{k}_{x,y}) = \frac{\hbar^2}{2m_{QW}} (k_x^2 + k_y^2); \quad \varphi \sim \exp(i\mathbf{k}_{x,y}\mathbf{r}_{x,y}) \quad (2.7)$$

The out-of-plane solutions are that of an electron in a finite QW, and the Hamiltonian must account for the potential profile $V(z)$. The wavefunctions of an electron in the ground state (ϕ_0) and in the first excited state (ϕ_1) are⁸⁹

$$\phi_0(z) \quad C_0 \begin{cases} e^{\alpha_0(z+a/2)} \cos\left(k_0 \frac{a}{2}\right) & z < -a/2 \\ \cos(k_0 z) & -a/2 \leq z \leq a/2 \\ e^{-\alpha_0(z-a/2)} \cos\left(k_0 \frac{a}{2}\right) & z > a/2 \end{cases} \quad (2.8.a)$$

$$\phi_1(z) \quad C_1 \begin{cases} -e^{\alpha_1(z+a/2)} \sin\left(k_1 \frac{a}{2}\right) & z < -a/2 \\ \sin(k_1 z) & -a/2 \leq z \leq a/2 \\ e^{-\alpha_1(z-a/2)} \sin\left(k_1 \frac{a}{2}\right) & z > a/2 \end{cases} \quad (2.8.b)$$

with $C_{0,1}$ being the normalization constants, and $\alpha_{0,1} = \sqrt{2m_b(\Delta E_c - E_{0,1})}/\hbar$ and $k_{0,1} = \sqrt{2m_{QW}E_{0,1}}/\hbar$ the wavenumbers in the barrier and in the QW, respectively. Note that the

wavefunction decays exponentially in the (Zn,Mg)O barriers and behaves as a sine/cosine in the ZnO QW. The parity of the wavefunctions in consecutive energy levels $\phi_n(z)$ and $\phi_{n+1}(z)$ of a symmetric QW alternates. The discrete energy levels E_n are obtained when the boundary conditions are applied at $z = \pm a/2$ to the wavefunctions in Eqs. 2.8.a and 2.8.b, and the term *subband* acquires its full meaning: the electrons have a discrete energy in z with different in-plane momenta, and the total energy is given by

$$E_{n,k} = E_n + \frac{\hbar^2}{2m_{QW}} (k_x^2 + k_y^2). \quad (2.9)$$

The occupation of the subband will depend on the number of electrons in the QW, i.e. on the Ga doping level of ZnO, and the number of subbands in the QW will depend on its thickness and the CB offset.

2.4.3. Intersubband transitions and selection rule

Considering a QW with two energy levels, receiving an external time-dependent electromagnetic field represented by the vector potential $\mathbf{A}(t)$, the interaction of the electromagnetic wave with an electron in the ground level is described by the Hamiltonian⁴¹

$$H_{per}(t) = \frac{e}{m_{QW}} \mathbf{A}(t) \cdot \hat{\mathbf{p}}, \quad (2.10)$$

where the second order term has been neglected, $\hat{\mathbf{p}}$ is the electron momentum operator and e the electron charge. Applying the electric dipole approximation, since the wavelength of the incoming radiation is much longer than the QW width, the vector potential is described by

$$\mathbf{A}(t) = \frac{E_0}{i\omega} (e^{-i\omega t} - e^{i\omega t}) \cdot \hat{\mathbf{e}}, \quad (2.11)$$

being $\hat{\mathbf{e}}$ the polarization unit vector and ω the frequency of the wave. The Fermi's golden rule for the transition rate from the state 0 to the state 1 induced by an external electromagnetic field is

$$W_{01} = \frac{2\pi}{\hbar} f_0(1 - f_1) |\langle \phi_1(z) | H_{per} | \phi_0(z) \rangle|^2 \delta(E_1 - E_0 - \hbar\omega), \quad (2.12)$$

where is $M = \langle \phi_1(z) | H_{per} | \phi_0(z) \rangle$ is the matrix dipole element and $f_{0,1}$ is the Fermi factor of the initial and final states. Combining W_{01} with Eqs. 2.10 and 2.11 results

$$W_{01} = \frac{2\pi}{\hbar} \left(\frac{eE_0}{m_{QW}\omega} \right)^2 |\langle \phi_1(z) | \hat{\mathbf{e}} \cdot \hat{\mathbf{p}} | \phi_0(z) \rangle|^2 \delta(E_1 - E_0 - \hbar\omega). \quad (2.13)$$

The $\hat{\mathbf{e}} \cdot \hat{\mathbf{p}}$ multiplication will dictate the polarization selection rule for the ISBT:

- In-plane polarization

$$\hat{\mathbf{e}} = (e_x, e_y, 0) \rightarrow \hat{\mathbf{e}} \cdot \hat{\mathbf{p}} = -i\hbar \left(e_x \frac{\partial}{\partial x} + e_y \frac{\partial}{\partial y} \right) \quad (2.14)$$

$$\langle \phi_1(z) | \hat{\mathbf{e}} \cdot \hat{\mathbf{p}} | \phi_0(z) \rangle = (\hbar k_x + \hbar k_y) \langle \phi_1(z) | \phi_0(z) \rangle = 0$$

There is no absorption when the incident electric field is in-plane polarized.

- Out-of-plane polarization

$$\hat{\mathbf{e}} = (0, 0, e_z) \rightarrow \hat{\mathbf{e}} \cdot \hat{\mathbf{p}} = -i\hbar e_z \frac{\partial}{\partial z} \quad (2.15)$$

$$\langle \phi_1(z) | \hat{\mathbf{e}} \cdot \hat{\mathbf{p}} | \phi_0(z) \rangle = -i\hbar e_z \left\langle \phi_1(z) \left| \frac{\partial}{\partial z} \right| \phi_0(z) \right\rangle \neq 0$$

There is absorption when the incident electric field is out-of-plane polarized.

Hence, the polarization selection rule must be satisfied for an ISBT to take place, and the selected geometry could play a major role in order to maximize the ISB absorption. In addition, there is another selection rule arising from the parity of the wavefunctions. In a symmetric QW with incident radiation out-of-plane polarized, the integral of the dipole matrix element vanish when the parity of the initial and final state wavefunctions is the same, since the operator $\hat{p}_z$ changes the parity of the wavefunction where it is applied. Then, in this situation, only transitions where subbands with different parity are involved are allowed.

2.4.4. Corrections

The above formulation of ISBTs is valid for a system where many particle interactions have been neglected. However, in many cases it is necessary to apply some corrections in order to consider the many particle interaction phenomena arising in a real system. In this thesis two of them have been considered: the Coulomb interaction between electrons and ionized dopants, and the interaction between electrons and the time-dependent incoming electromagnetic field.

Coulomb correction

The electrons in the ZnO:Ga QW, with negative charge, and the Ga-ionized dopants, with positive charge, bend the CB potential profile, modifying the energy and wavefunctions of the subbands in the QW. This effect can be considered with the Poisson's equation, as

$$\frac{\partial^2 V(z)}{\partial z^2} = \frac{e^2}{\varepsilon} [N_D^+(z) - n_{2D}\phi^*(z)\phi(z)], \quad (2.16)$$

where e is the electron charge, ε is the vacuum permittivity multiplied by the material dielectric constant, $N_D^+(z)$ is the density of ionized dopants, and n_{2D} is the 2D electron concentration. The first term of the right-hand side in Eq. 2.16 accounts for the bending of the CB produced by the ionized dopants, and the second term accounts for the inhomogeneous distribution of the electrons in the QW.

Since the Poisson's equation modifies the CB profile along the z -axis and therefore the wavefunctions, it needs to be solved self-consistently together with the Schrödinger equation.

Depolarization shift

Due to the high electron concentrations in the ZnO:Ga QWs, the most important correction to be done is the dynamic-interaction between the electrons and the incident IR radiation, the so-called depolarization shift.⁹⁰ The electrons in the QW feel the time-dependent external radiation and the layer is polarized, leading to surface charge densities and creating a depolarization field. Thus, the effective field in the layer is modified and therefore the energy required to promote an electron from the ground state to the excited state is blue-shifted an amount proportional to the plasma frequency (ω_p), i.e. proportional to the square root of the three-dimensional free electron concentration (n) in the layer, since⁴³

$$\omega_p = \sqrt{\frac{ne^2}{m_e^* \varepsilon_0}}, \quad (2.17)$$

where ε_0 is the vacuum permittivity.

In 1976, Chen *et al.*⁹¹ proposed a simple model consisting of a thin slab with an anisotropic dielectric function to deal with the ISB absorption, and the zero of the out-of-plane dielectric function was calculated at

$$\tilde{\omega}_{01}^2 = \omega_{01}^2 + f_{01}\omega_p^2, \quad (2.18)$$

where ω_{01} is the difference in frequency between the subbands, and $f_{01}\omega_p^2$ is the depolarization shift, being f_{01} the oscillator strength of the transition.

2.4.5. Quantum cascade lasers and quantum well infrared photodetectors

The concept of quantum cascade has its origin in the 1970s, when Esaki and Tsu published their results about tunneling transport in superlattices⁹² and Kazarinov and Suris suggested optical gain in 2D heterostructures.⁹³ The principle of operation of quantum cascade lasers (QCLs), schematized in Figure 2.7, relies on these two quantum phenomena: the tunneling transport of electrons through a barrier in the CB and the recombination of these electrons from the upper subband to the lower subband in the QW. The difference in energy from different subbands in a QW could be from a few mili- to hundreds of eV, depending on the design of the superlattice, which is a great advantage with respect to other sources with discrete energy outputs, allowing to extend the radiation from the mid-IR to the THz.

Figure 2.7. Representation of the structure of a quantum cascade laser.

In QCLs, electrons are injected in the upper subband (subband 3 in Figure 2.7) by tunneling, through a miniband formed in the multiple quantum well injector. Electrons in subband 3 experiment a radiative recombination to subband 2 emitting photons efficiently. The strength of the transition, and therefore the gain, is affected by the population inversion between subbands 2 and 3. In order to maintain subband 2 depopulated, electrons undergo a phonon-assisted transition from subband 2 to subband 1, with a lower recombination rate than the radiative transition. Then, electrons are injected again through a miniband to the following subband 3'.

The main drawback of GaAs-based QCLs is the low energy of the LO phonon in GaAs (36 meV),⁹⁴ which prevents the design of efficient GaAs-QCLs in the THz. As explained with Figure 2.8, the low LO-phonon energy, comparable with the energy of the transition from subband 3 to 2, enables electrons in the upper subband to undergo a phonon-assisted non-radiative transition to the lower subband, especially for temperatures approaching the room temperature. However, the ZnO LO-phonon energy doubles that of GaAs (72 meV) so the phonon-assisted non-radiative recombination is suppressed, allowing the design of potential QCLs working in the THz at higher temperatures.

Figure 2.8. Schematic representation of radiative and non-radiative allowed processes in GaAs and ZnO quantum cascade lasers.

On the other hand, the first demonstration of a working QWIP was in 1987 by Levine *et al.*,⁹⁵ detecting a photoresponse at $\lambda = 10.8 \mu\text{m}$ in a GaAs-based multiple quantum well superlattice.

In order to design a QWIP, several parameters need to be considered. In bound-to-bound state QWIPs, as those designed in this thesis, photogenerated current

comes from the absorption of photons by electrons in the ground state of the doped-QW, which are photo-excited to the upper state and then tunnel out of the well when an external bias is applied. Typically, QWs are designed so that the excited state is close to the resonance with the continuum, thus increasing the escape probability of photo-excited electrons. The dark current has two main contributions: electrons tunneling between the ground states of adjacent QWs and electrons thermally-emitted from the QW.⁹⁶ The former contribution can be reduced with a proper width of the barriers, while the later will depend on the relative position of the ground and excited states to the barrier and on the system temperature.

2.5. (Cd,Zn)O transparent conductive oxides for plasmonic applications

2.5.1. Modelling the dielectric function with the Drude model

In metals and conductive semiconductors, such as CdO, the dielectric function $\varepsilon(\omega)$ is well reproduced in the mid-IR by the Drude model, in the form of

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_p}, \quad (2.19)$$

where ε_{∞} is the high-frequency dielectric constant and γ_p the damping term of the plasma frequency ω_p . The real and imaginary parts of the dielectric function in Eq. 2.19 and the energy loss function, defined as $Im[-1/\varepsilon(\omega)]$, are shown in Figure 2.9.

Figure 2.9. Real and imaginary parts of the dielectric function defined by the Drude model (Eq. 2.19) and energy loss function.

When the frequency of the incoming radiation is $\omega < \omega_p$, the real part of the dielectric function is negative and the wave is attenuated in the medium, i.e. no radiation can propagate on it. At the plasma frequency the dielectric function of the material vanishes and corresponds to the oscillation frequency of free electrons. As predicted by the energy loss function (Figure 2.9), at that frequency electrons absorb the incoming radiation, inducing a minimum in the reflectance spectra. This can be explained with the Maxwell equations.⁹⁷ The displacement vector $\mathbf{D}$ of the medium is given by

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} = \epsilon_0 \epsilon(\omega) \mathbf{E}, \quad (2.20)$$

where $\mathbf{P}$ is the polarization vector and $\mathbf{E}$ the electric field. At the plasma frequency $\text{Re}[\epsilon(\omega_p)] = 0$, and in order to satisfy Eq. 2.20, the polarization of the metal $\mathbf{P}$ is in the opposite direction than the depolarization field $\mathbf{E}$,

$$\epsilon_0 \mathbf{E} = -\mathbf{P} \quad (2.21)$$

Thus, the plasma frequency could be interpreted as the collective longitudinal oscillation of the free electrons in the medium, which produces a polarization field $\mathbf{P}$ along the propagation direction, and a depolarization field $\mathbf{E}$ in the opposite way. At the interface between the CdO and the adjacent medium, the longitudinal oscillation produces dipole, resulting in a sharp minimum visible in the p -polarized reflectance spectrum (see Appendix B).

In typical noble metals as Au, the plasma frequency falls in the VIS-UV regimes of the electromagnetic spectra. However, in semimetals as the (Cd,Zn)O alloy, $n \sim 1 \times 10^{20} \text{ cm}^{-3}$ and the plasma frequency falls in the mid-IR and can be modulated with the Zn content, improving the prospects of the alloy as a plasmonic material for the mid-IR region.

2.5.2. Surface plasmon polariton

The interaction between light and matter in the (Cd,Zn)O ternary is studied in Chapter 7, and the available eigenstates satisfying the Maxwell equations are the polaritons. Polaritons are quasiparticles composed of photons and elementary matter excitations, such as plasmons or phonons. Note that in this subsection and when referring to polaritons along this thesis, $\mathbf{k}$ stands for the polariton momentum, a nomenclature commonly accepted in the literature (indeed the momentum $\mathbf{p}$ is proportional to $\mathbf{k}$ through $\mathbf{p} = \hbar \mathbf{k}$).

The surface plasmon polariton (SPP) is a solution of the Maxwell equations in which an electromagnetic wave propagates along the interface between a dielectric and a conductive medium, in this thesis the (Cd,Zn)O alloy, and it decays exponentially in the direction normal to the interface. The SPP can be excited only when the incident electromagnetic wave has a component of the electric field transversal to the interface.⁴³ Taking $z = 0$ at the (Cd,Zn)O-dielectric interface, the components of the potential vector $\mathbf{H}$ and electric field $\mathbf{E}$ have the form

$$\begin{aligned}
 & \left. \begin{array}{l} z > 0, \text{ dielectric} \\ \\ \\ \end{array} \right\} \begin{cases} H_y(z) = A_2 e^{ik_x x} e^{-k_{z,2} z} \\ E_x(z) = iA_2 \frac{k_{z,2}}{\omega \epsilon_0 \epsilon_2} e^{ik_x x} e^{-k_{z,2} z} \\ E_z(z) = -A_2 \frac{k_x}{\omega \epsilon_0 \epsilon_2} e^{ik_x x} e^{-k_{z,2} z} \end{cases} \quad (2.22.a) \\
 & \left. \begin{array}{l} z < 0, \text{ (Cd,Zn)O} \\ \\ \\ \end{array} \right\} \begin{cases} H_y(z) = A_1 e^{ik_x x} e^{k_{z,1} z} \\ E_x(z) = -iA_1 \frac{k_{z,1}}{\omega \epsilon_0 \epsilon_1} e^{ik_x x} e^{k_{z,1} z} \\ E_z(z) = -A_1 \frac{k_x}{\omega \epsilon_0 \epsilon_1} e^{ik_x x} e^{k_{z,1} z} \end{cases} \quad (2.22.b)
 \end{aligned}$$

where A_1 and A_2 are amplitude constants, k_x is the in-plane momentum of the surface polariton and $k_{z,1}$ and $k_{z,2}$ the out-of-plane momenta in the (Cd,Zn)O and dielectric, respectively. Note that for simplicity, the dependence in ω of the dielectric function of the (Cd,Zn)O is not indicated, i.e. $\epsilon_1(\omega) \equiv \epsilon_1$. The electric field distribution at the (Cd,Zn)O-dielectric interface when a SPP is excited is represented in Figure 2.10.

Figure 2.10. (a) Electric field distribution of a SPP at the (Cd,Zn)O-dielectric interface and (b) module of the z -component of the electric field and its penetration depth in both media.

Applying boundary conditions at the interface, the following dispersion relation is obtained

$$k_x = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}, \quad (2.23)$$

valid for real and imaginary ε_1 and ε_2 . The out-of-plane momenta in both media will be then

$$k_{z,i} = k_0 \sqrt{\frac{\varepsilon_i^2}{\varepsilon_1 + \varepsilon_2}}, \quad \text{with } i = 1, 2. \quad (2.24)$$

Since the surface polariton is propagating along the interface in the $+x$ direction, $Re\{k_x\}$ must be positive. Also, the wave decays in the $\pm z$ direction, and then $Re\{k_{z,i}\}$ must be positive. From Eqs. 2.23 and 2.24, these two conditions become

$$\begin{aligned} Re\{\varepsilon_1\}Re\{\varepsilon_2\} &< 0 \\ Re\{\varepsilon_1\} + Re\{\varepsilon_2\} &< 0. \end{aligned} \quad (2.25)$$

Then, for the propagation of a surface polariton to be possible, the real part of the dielectric function of medium 2 is required to be positive whereas that of medium 1 negative (or *vice versa*). As discussed in the previous section, the real part of the dielectric function of the (Cd,Zn)O (medium 1 in Figure 2.10) is negative when $\omega < \omega_p$.

The dispersion curve given by Eq. 2.23 is plotted in Figure 2.11 for an interface between air and a lossless (Cd,Zn)O. The lower branch in Figure 2.11 is the SPP, also known as the Fano mode,⁴² which for $Re\{k_x\} \rightarrow 0$ approaches the light line in air and for $Re\{k_x\} \rightarrow \infty$ approaches the ω_{SPP} asymptote. This asymptote can be obtained from Eq. 2.23, and results

$$\omega_{SPP} = \frac{\omega_p}{\sqrt{\varepsilon_{\infty,2} + \varepsilon_{\infty,1}}}, \quad (2.26)$$

in a lossless (Cd,Zn)O, where $\varepsilon_{\infty,2} = 1$ and $\varepsilon_{\infty,1} = 5.1$ in an air-(Cd,Zn)O interface. Then, the asymptote not only depends on the high-frequency dielectric constant of the (Cd,Zn)O but also on that of the adjacent medium.

Figure 2.11. Dispersion curve of a lossless plasmon polariton, with the upper branch corresponding to the Brewster mode or radiative mode, and the lower branch corresponding to the Fano mode or surface mode. The horizontal dotted lines indicate the plasma frequency (ω_p) and the asymptote of the Fano mode at high in-plane momenta (ω_{SPP}). The red tilted line indicates the asymptote of the Brewster mode, with slope $\sqrt{\epsilon_{\infty,1} \cdot \epsilon_{\infty,2} / (\epsilon_{\infty,1} + \epsilon_{\infty,2})}$, and the green tilted line indicates the light line in air, with slope 1.

On the other hand, the upper branch in Figure 2.11 is the interface plasmon polariton (see Appendix B for more details about bulk and interface polaritons in semiconductors), also known as the radiative mode or Brewster mode,⁴² since it lies at the left of the light line and it can leak in the dielectric. It starts at ω_p for low values of $Re\{k_x\}$ and then, as $Re\{k_x\}$ is further increased, it approaches the asymptote with slope $\sqrt{\epsilon_{\infty,1} \cdot \epsilon_{\infty,2} / (\epsilon_{\infty,1} + \epsilon_{\infty,2})}$, easily obtained from Eq. 2.23. In the region of frequencies between ω_{SPP} and ω_p light cannot propagate within the (Cd,Zn)O.

However, once the losses are considered through the damping term γ_p , the in-plane momentum k_x becomes a complex number with $Im[k_x] \neq 0$. The direct consequence is the restriction of the propagation of the surface wave to the so-called propagation length, defined as

$$L_p = \frac{1}{2Im[k_x]}. \quad (2.27)$$

The damping term introduces also slight changes in the dispersion curve of the surface polariton: the constraint of the plasmonic bandgap (the region of frequencies between ω_{SPP} and ω_p where light cannot propagate) is relaxed, and k_x does not diverge at ω_{SPP} , connecting the Fano mode with the Brewster mode.

Chapter 3. Characterization and processing techniques

In this chapter, the fabrication steps of the devices involved in the thesis will be first described, followed by the optical and electrical characterization techniques employed for the analysis of the devices and the samples.

3.1. Sample preparation and device fabrication

3.1.1. Material Growth

The samples analyzed in this thesis were grown in two institutions:

- Alloys based on ZnO, part of the European ZOTERAC project, were grown at the *Centre National de la Recherche Scientifique*, by the group of J.-M. Chauveau. The samples were grown by MBE on *m*-plane native ZnO substrates and *m*-plane sapphire substrates.
- Alloys based on CdO, part of Spanish national projects TEC2014-60173-C2-2 and TEC2017-85912-C2-1-R, were grown at the Crystal Growth and Characterization of Semiconductors group of Prof. Vicente Muñoz Sanjosé from *Universitat de València*. The samples were grown by MOCVD on *r*-plane sapphire substrates.

3.1.2. Device Processing

Three different processing procedures were developed throughout this thesis. First, in order to maximize the measured ISB absorption in ZnO:Ga/(Zn,Mg)O multiple quantum wells, samples have to be polished in a multipass waveguide geometry. Secondly, the characterization of quantum well infrared photodetectors requires the processing of the ZnO:Ga/(Zn,Mg)O samples. Finally, for measuring capacitance-voltage (CV) profiles Schottky diodes have to be processed.

Processing of beveled waveguides and substrate back surfaces

There was no previous experience on polishing ZnO at ISOM, so the procedure was optimized at the beginning of the thesis. Samples are required to be polished in two situations. For regular transmittance measurements the back surface of the sample needs to be polished, otherwise, its roughness will produce light scattering with the consequent optical losses. The surface roughness of the back-surface of a ZnO sample is shown in Figure 3.1.

Figure 3.1. (a) Depth profiles of the surface of a ZnO substrate and (b) a Nomarsky microscope picture of the same surface before and after being polished.

The measured root mean square surface roughness before polishing was ~ 600 nm and after being polished ~ 10 nm (Figure 3.1 (a)). Also, the Nomarsky pictures (Figure 3.1 (b)) reveal a good optical quality of the polished surface although some residual stripes formed during the process are still visible. The effect polishing has on the IR transmittance spectra of a ZnO substrate is shown in Figure 3.2.

Figure 3.2. IR transmittance spectra of a ZnO substrate before and after being polished.

Light scattering has a considerable effect causing a drop in the transmitted signal, especially for larger frequencies, whose wavelengths are in the order of the unpolished

surface grains. In Figure 3.2 it is also observed the effect of phonons that absorb and reflect light for frequencies below $\sim 1200 \text{ cm}^{-1}$.

On the other hand, to fulfill the ISB selection rules and enhance its absorption strength, a beveled waveguide needs to be optimized, as schematized in Figure 3.3. The surface of the bevel forms 45° with the surface of the MQWs, and IR light is coupled normal to it. Thus, light passes several times through the MQWs, depending on the thickness and length of the waveguide.

Figure 3.3. 45° multipass waveguide geometry for transmittance measurements.

Samples were polished mechanically with a set of grinding foils and clothes with polycrystalline diamond particles. The samples are polished with a LaboPol-4 polishing system from Struers. Samples are fixed to a metallic holder with wax and loaded in a turntable. Then, they are placed in contact with the grinding foils and clothes at the desired angular speed. Luckily, ZnO is not a hard material (4.5 in the Mohs scale⁹⁸) and it can be easily polished with SiC grinding foils. First, grinding foils with a larger surface roughness are used, of about 25 to $15 \mu\text{m}$ (from # 800 to # 1200 of the Federation of European Producers of Abrasives grain scale), depending on the thickness of material to remove. Then the grain size of the SiC grinding foils is reduced step by step, with a final grain size of $3 \mu\text{m}$ (# 4000). Once the last SiC grinding foils is used, several clothes are employed for the final steps. Each cloth contains an aqueous solution with polycrystalline diamond particles, from an average size of $9 \mu\text{m}$ down to a final average size of $0.25 \mu\text{m}$. In between each step, the samples are carefully cleaned to avoid dragging particles to the next step.

The procedure to polish the samples in the 45° multipass waveguide geometry is similar. In this case, a metallic holder with an indentation at 45° is employed, as shown in Figure 3.4. The sample is placed on it and covered with wax. Then, the holder with the sample is put in the turntable to start the polishing process.

Figure 3.4. (a) Picture of the holder employed to polish the 45° multipass waveguides with an indentation at 45° and (b) schematic of the sample in the holder covered with wax ready to be polished.

Processing of QWIPs

The procedure to process ZnO devices was first developed by Dr. Gema Tabares,⁹⁹ showing excellent results, and improved by Dr. Alejandro Kurtz.¹⁰⁰ The steps for QWIP processing are schematized in Figure 3.5 and described below. A picture of a processed sample is shown in Figure 3.6.

Figure 3.5. Steps for processing quantum well infrared photodetectors. Not to scale.

Figure 3.6. (a) Nomarsky microscope top-view picture of processed QWIPs, and (b) encapsulated sample with QWIPs and beveled surface in a TO-8 ready to be tested.

Preparing the sample

- Cutting and cleaning. The sample is cut in a $3 \times 5 \text{ mm}^2$ piece, big enough to contain several devices on it. This step is followed by the sample cleaning in acetone and isopropanol that allows to eliminate impurities affecting the photolithography processes.

Extended ohmic contact

- First photolithography (Figure 3.5 (1)). Circular resist patterns are defined with a diameter of $200 \mu\text{m}$ that define the mesa ohmic contacts of the devices.
- Wet chemical etching (Figure 3.5 (2)). The sample is etched with H_3PO_4 diluted in deionized water to a final concentration of 0.1 % in volume, ensuring an etching speed of about 40 nm/min and a good control of the final mesa depth. The circular resist patterns protect the surface of the top contact.
- Extended ohmic contact deposition and annealing (Figure 3.5 (3)). Once the desired mesa depth is achieved, a multilayered metal deposition is done in an electron beam evaporator. The metal layers are Ti-Al-Ti-Au, with thicknesses of 20-100-40-140 nm, respectively, assuring a good surface adherence. Following this step, a lift-off is performed to remove the resist and metal from the circular patterns. In order to reduce the contact resistance and diffuse the metal into the semiconductor, an annealing is done under high vacuum conditions ($\sim 10^{-4} \text{ mbar}$). This annealing has been improved respect to the previous procedure available in

the group where an atmosphere with a mixture of H_2 and N_2 (95 % H_2 , 5 % N_2) was used. However, it has been observed that H may introduce donors in oxides such as ZnO and CdO increasing the residual electron concentration. Thus, the annealing under vacuum conditions allows to avoid the impact of diffused H. The annealing is done for 1 minute at 20 °C below the growth temperature, in order to minimize potential crystal structural changes in the sample.

Mesa ohmic contact

- Second photolithography (Figure 3.5 (4)). The extended ohmic contact is covered with resist in order to define the mesa contact.
- Mesa ohmic contact deposition and annealing (Figure 3.5 (5)). Similarly to the ohmic contact, a multilayered metal deposition is performed, followed by the corresponding lift-off process to remove the resist and metal from the ohmic contact. The shape of the negative of the top contact has the Pac-Man style, previously designed by A. Kurtz,¹⁰⁰ in case light needs to be coupled from the window on top. The top contact is annealed with the same conditions as the ohmic contact.

Mounting the sample

- Beveling the sample (Figure 3.5 (6)). A 45° bevel is polished in one of the edges of the sample in order to couple IR light on it, trying to maximize the number of accessible devices to be measured. This step is also new with respect to the previous recipe and necessary to maximize the coupled light into the QWIPs. Since the devices are already processed, special care has to be taken when polishing and cleaning the sample.
- TO-8 encapsulation. The sample with the processed devices is mounted in a TO-8, which will serve as the holder with which the electrical circuit will be accessed. In order to isolate electrically the sample from the holder, a small piece of sapphire is fixed with epoxy between the device and the TO-8 holder.
- Wire bonding. The electrical access is achieved by means of wire bonding with Au micro-wires. The bonding is done in a ball wire bonding system, which applies ultrasonic vibrations and heat in order to bond the previously formed Au ball to the contact of the device.

Processing Schottky diodes for capacitance-voltage profiling

Some of the steps for processing Schottky diodes are the same as for processing QWIPs, with a few differences, since the Schottky diodes processed along this thesis are planar and their rectifying behavior is very sensitive to the quality of the metal-semiconductor interface (see Section 3.5). The ZnO surface that will be below the metal and form the Schottky junction has to be passivated: the presence of defects and charge accumulation on the surface makes it necessary to do a previous treatment with H_2O_2 , which has been proved to passivate the surface forming a thin ZnO resistive layer.^{101,102} As a result, the accumulated charge is reduced, lowering the band bending and improving the rectification behavior of the Schottky diodes.^{103,104} The steps for processing Schottky diodes are schematized in Figure 3.7 and described below.

Figure 3.7. Steps for processing Schottky contacts. Not to scale.

Preparing the sample

- Cutting and cleaning. Same procedure as for QWIPs.

Extended ohmic contact

- First photolithography (Figure 3.7 (1)). Circular resist patterns are defined.
- Extended ohmic contact deposition and annealing (Figure 3.7 (2)). Same procedure as for the extended ohmic contact in QWIPs.

Schottky contact

- Second photolithography (Figure 3.7 (3)). The extended ohmic contact is covered with resist in order to protect it. Before the H_2O_2 treatment, the resist is hardened with heat.
- H_2O_2 treatment (Figure 3.7 (4)). The sample is immersed in H_2O_2 boiling at 100 °C to passivate the surface. Then it is important to avoid a long air exposure of the passivated surface, in order to avoid contamination, so the sample is immediately loaded in the vacuum chamber of the electron beam evaporator, where the Schottky contact will be deposited.
- Schottky contact deposition (Figure 3.7 (5)). A 100-nm Au layer is deposited on the circular exposed areas. After that, the lift-off process is done. The shape of the Schottky contact is a circle since for measuring CV curves no light needs to be coupled on the device.

3.2. Fourier transform infrared spectroscopy

The intersubband and plasmonics phenomena studied in this thesis fall in the mid-IR range of the electromagnetic spectrum, and thereby the Fourier transform infrared (FTIR) spectrometer is the most utilized set up along the thesis. This technique has some advantages with respect to other IR spectrometers:¹⁰⁵

- It allows to measure a full IR spectrum at once.
- It can achieve a signal-to-noise ratio comparable to that of an IR dispersive spectrometer.
- Ensures a constant and high spectral resolution in the whole spectral region.
- The aperture at the entrance of the detector is much higher than the slit in a grating spectrometer, ensuring a higher signal collection.
- It is non-invasive.

A Magna-IR 760 FTIR spectrometer is used in this thesis, and a scheme of it is shown in Figure 3.8. The operation principle of the spectrometer is based on a two-beam interferometer. Emitted IR light from a resistively heated SiC rod, is collimated and split in two paths with a KBr beam splitter. One of the beams reflects in a fixed mirror and the other in a moving mirror. Then, the IR beams are joined again, forming an interference

pattern which contains the information of all the frequencies, guided to the sample compartment and finally to the DGTS detector. When the Fourier Transform is applied to the interference pattern a full IR spectrum is obtained.

Figure 3.8. Schematic of the Magna-IR 760 FTIR spectrometer and its components. Taken from the user's guide (Ref. 106).

In order to get a transmittance or reflectance spectrum of the sample to be characterized, first a background is measured. The background includes the spectrum of the SiC lamp, slightly modified by the mirrors, beam splitter and absorption by the air in the compartment of the sample. Once the background has been recorded, the signal transmitted or reflected by the sample is measured and divided by the background.

The spectrometer has a N_2 purging system, in order to evacuate the atmospheric gases from the sample compartment and avoid their absorption. Some raw spectra (or backgrounds) of the SiC lamp with different N_2 purge levels are shown in Figure 3.9. In the inset the evolution of the CO_2 absorption peak for increasing N_2 purge level is shown, from a nearly total absorption to a nearly flat spectrum. Note that in the surface of the mirrors and beam splitter there are H_2O and CO_2 molecules adsorbed, among others, and therefore a complete elimination of the atmospheric peaks appearing in the spectrum is not possible. However, the N_2 purge level is not as important as having the same purge level both in the background and in the measured spectrum, in order to cancel the absorption peaks.

Figure 3.9. Spectra of the SiC lamp of the FTIR spectrometer for different N_2 purge levels. The inset shows in more detail the evolution of the CO_2 absorption peak.

The most common units used in FTIR spectroscopy for representing the spectra are inverse centimeters, and then, along the thesis, FTIR spectra are also presented with them. The source, together with the beam splitter, mirrors, and detector, give a measuring range from 350 to 9000 cm^{-1} .

In the thesis, the FTIR spectrometer has been used to characterize the samples in the mid-IR in different configurations, detailed below. In order to linearly polarize the light and set the polarization axis for each experiment, a wire grid polarizer can be placed at the entrance of the sample compartment.

3.2.1. Transmission configuration

Transmittance measurements can be carried out in order to determine the signal transmitted through a sample or a substrate and detect inhomogeneities. To do so, the back surface of the sample needs to be polished, to avoid light scattering, as shown before in Figure 3.2.

Besides, transmittance measurements were carried out in the 45° multipass waveguides, previously prepared as described in Section 3.1.2. These measurements were performed to detect the ISBTs in the ZnO multiple quantum wells, where, thanks to the

multiple passes through the active region, the absorbed signal increased. In order to check whether the ISBT selection rules are satisfied or not, a polarizer is employed.

3.2.2. Reflection configuration

Reflectance measurements provide useful information about the dielectric function of the material. In order to carry out reflectance measurements, a reflectance accessory is mounted in the sample compartment. The accessory guides the IR light with a set of mirrors to the surface of the sample and then to the detector, as represented in Figure 3.10.

Figure 3.10. Scheme of the accessory used in reflectance measurements.

The reflectance accessory allows to measure reflectance in the range of angles of incidence from 30° to 80° . First, the background is collected with a reference Au-mirror, and then the sample is measured to compare its reflected signal with that of the mirror signal. The reflectance accessory has an adapter for the N_2 -purging system to be connected, and the polarizer can be also placed at the entrance to set the polarization axis of the electric field. This allows to measure reflectance in *s*- and *p*-polarizations, depicted in Figure 3.11, whose convention is used throughout this thesis.

Figure 3.11. Schematic of the geometry for reflectance measurements in (a) *s*- and (b) *p*-polarizations of the incident light.

In *s*-polarization (also known as Transverse Electric), the electric field lies perpendicular to the plane of incidence whereas in *p*-polarization (also known as Transverse Magnetic) the electric field lies parallel to it. Thus, light-matter excitations that require a component of the electric field transversal to the interface can only be excited in *p*-polarization.

Attenuated total reflectance

Some light-matter interaction phenomena, such as the surface plasmon polariton (SPP), are only observable when the momentum of the light is matched to the polariton momentum, and it requires the employment of momentum matching techniques. In this thesis, in order to observe the SPP, a ZnSe prism with an internal angle of 45° and a high refractive index of about 2.37 has been used, as schematized in Figure 3.12.

Figure 3.12. Attenuated total reflectance geometry, with a ZnSe prism with an internal angle of 45° .

The prism is mounted on the reflectance accessory and the angle of incidence in the prism (α in Figure 3.12) can be selected from 30 to 80° as in conventional reflectance measurements. Due to light refraction, the angle of incidence in the prism-air interface (θ in Figure 3.12) can be varied between 39 and 59° . Precisely at the prism-air interface is where the total internal reflection occurs, due to the large difference between the refractive indexes of prism and air. The originated evanescent wave reaches the surface of the sample and excites the surface mode. The air gap between the prism and the surface of the sample can be reduced by applying pressure to the sample.

3.2.3. Photocurrent configuration

The photoresponse of the QWIPs can be measured also in the FTIR spectrometer. Processed and encapsulated QWIPs (see Section 3.1.2) are mounted in a cryogenic system, with a closed He circuit, where He in the gas phase is repeatedly compressed and expanded in order to extract heat from the cavity. Hence, the temperature is lowered to 10 K to reduce the dark current. A scheme of the mounted circuit is shown in Figure 3.13.

The IR source is the SiC rod from the FTIR spectrometer, and the IR beam is coupled to the beveled mirror of the processed sample, after passing through the polarizer. A maximum of 4 devices can be accessed at once, so first current-voltage (IV) curves are measured at room temperature and those devices with lower dark current are selected. Each device is biased individually at low voltages (5 V max.), in order to collect the photogenerated current. Then, the current is driven to a converter with a pre-selected gain, which turns it into voltage. Finally, the voltage signal is fed back to the voltage input of the FTIR spectrometer, and in the computer the interference pattern is visualized.

Figure 3.13. Scheme of the mounted circuit for measuring photocurrent in QWIPs.

3.3. Ultraviolet-visible absorption spectroscopy

The bandgap of the oxides studied in this thesis falls in the UV-VIS regions of the electromagnetic spectrum. Thus, the optical bandgap can be analyzed by means of UV-VIS absorption spectroscopy. To do so, a Jasco V-650 spectrophotometer is used, which has one monochromator and two different light sources to cover the spectrum from 190 to 900 nm: a Deuterium lamp from 190 to 350 nm and an Halogen lamp from 330 to 900 nm.

This technique does not require sample preparation, and two corrections are performed for each transmission spectra: dark correction and baseline correction. First, a spectrum in dark conditions without the holder and the sample is measured, in order to detect the possible residual light lines within the sample's compartment. Then the baseline is measured with the holder of the sample, which considers the possible artefacts introduced by the holder and any other element apart from the sample present where the sample is fixed. Finally, the holder with the sample on it is measured, and ideally the final spectrum corresponds to the transmitted signal through the sample.

3.3.1. Optical bandgap

Once the transmitted spectrum is recorded, the absorption coefficient (α) of the layer is calculated with Eq. 3.1, assuming the reflection of the sample is negligible. Following the Beer-Lambert law, light intensity after passing through a layer with thickness d is

$$I(d) = I_0 e^{-\alpha d}, \quad (3.1)$$

where I_0 is light intensity before impinging the sample. The absorption coefficient gives information about the interband transitions of the material. The relation between α and the optical bandgap of the material (E_g^{opt}) is then given by

$$\alpha(h\nu) = A \frac{(h\nu - E_g^{opt})^n}{h\nu}, \quad (3.2)$$

where $h\nu$ is the photon energy, A is a factor related to the effective mass (see Chapter 3 of Ref. 107), and n takes a value of 0.5 for direct allowed transitions and 2 for indirect allowed transitions.¹⁰⁷ Thus, fitting Eq. 3.2 in a Tauc plot¹⁰⁸ the optical bandgap can be determined.

3.3.2. Burstein-Moss shift and bandgap renormalization

In semiconductors with high electron densities, the optical bandgap of the material E_g^{opt} may not be equal to the real bandgap E_g , as illustrated in Figure 3.14, and some corrections have to be done to obtain the latter.

Figure 3.14. (a) Optical bandgap and real bandgap in a non-degenerate semiconductor, and (b) in a degenerate semiconductor where the Burstein-Moss shift is present.

When a semiconductor is doped with atoms acting as donors, the Fermi level (E_f in Figure 3.14) approaches the CB minimum. If the donor concentration is further increased the Fermi level may exceed the CB minimum, and the semiconductor becomes degenerate. In this situation, the optical bandgap measured by means of absorption spectroscopy is larger than the real bandgap, as in Figure 3.14 (b), since there are no available free states at the CB minimum.

This blue-shift produced by the band filling is known as the Burstein-Moss shift,⁶⁴ and can be calculated with

$$E_{BM} = \left(\frac{\hbar^2}{2m_e^*} \right) (3\pi^2 n)^{\frac{2}{3}}. \quad (3.3)$$

Then, the optical bandgap is the real bandgap added to the Burstein-Moss shift, as

$$E_g^{opt} = E_g + E_{BM}. \quad (3.4)$$

On the other hand, for large donor and electron concentrations, many-body effects such as electron-electron and electron-impurity interactions could arise,⁵⁰ inducing a band-gap renormalization, which tends to lower the optical bandgap.

3.4. Hall effect measurements

The Hall effect technique is a very useful tool to obtain the electrical characteristics of the sample. In this thesis, Hall effect is measured in the Van der Pauw configuration¹⁰⁹ at room temperature. Samples are cut in $5 \times 5 \text{ mm}^2$ pieces, and then 200 nm-thick Au contacts are deposited at the surface of the corners of the sample with an electron beam evaporator. Then, the contacts are annealed for 1 minute to reduce the contact resistance and increase the adherence. Finally, the sample is fixed with epoxy to a chip holder and the Au-contacts are wire-bonded to the chip-paths, as shown in Figure 3.15 (b).

Figure 3.15. (a) Scheme of the Hall configuration for measuring the Hall voltage, and (b) a Nomarsky microscope picture of the mounted and wire-bonded sample. Note the lateral dimension of the sample is 5 mm.

First, the resistivity (ρ) of the sample is measured by applying current between two consecutive corners with a Keithley 220 current source, and measuring the voltage drop between the two opposite corners with a Keithley 195 multimeter. This step is repeated along the four edges of the sample, and with positive and negative current flow directions, allowing to reduce the error bar due to the small differences in the geometry and possible inhomogeneities on the conductive layer. It is worth to note that in the Van der Pauw configuration the main source of error comes from the finite size of the contacts (c) compared to the edge length (l), as¹⁰⁹

$$\frac{\Delta\rho}{\rho} \propto \left(\frac{c}{l}\right)^2 \quad (3.5)$$

Thus, the size of the contacts is limited to about 0.5 mm, one order of magnitude lower than the edge length of the sample, and the resistivity relative error is reduced to $\sim 1\%$.

Once the resistivity is known, the Hall voltage is measured in two configurations. The sample is loaded between the poles of an electromagnet connected to a Sorensen current source. The magnetic field is applied perpendicular to the surface of the sample, and then a current flow is established in the diagonal 1 – 3 of the sample (Figure 3.15 (a)). The Lorentz force drives a charge separation in a direction perpendicular to both the magnetic field and the current flow directions, i.e. in the diagonal 2 – 4. This generates an electric field opposing the Lorentz force. When the electric force equals the Lorentz force, the Hall voltage in the diagonal 2 – 4 is

$$V_H = \frac{I \cdot B}{-n_{Hall} \cdot e \cdot d}. \quad (3.6)$$

The only unknown variable in Eq. 3.6 is the Hall electron concentration. This measurement is repeated in the other available configuration (with the current flow established in the 2 – 4 diagonal and the Hall voltage measured in the 1 – 3 diagonal), and both with positive and negative magnetic field and current flow, again to reduce the error bar and avoid geometric inhomogeneities.

The resistivity of the sample is defined as

$$\rho = \frac{1}{e \cdot n \cdot \mu} \quad (3.7)$$

where μ is the electron mobility. Since the electrical resistivity was previously measured and the electron concentration is derived from the Hall voltage, it is straightforward to obtain the electron mobility. Thus, the transport characteristics of the sample are determined.

The Hall effect technique is very useful and reliable when the electron concentration to be measured is above $\sim 10^{18} \text{ cm}^{-3}$. For lower electron concentrations there are some limitations. The required voltage to establish a current flow increases with the resistance of the layer and the breakdown voltage may be reached. One possibility to avoid approaching the breakdown voltage is to reduce the current flow. However, then the Hall voltage would be reduced (Eq. 3.6) and the error bar increases.

3.5. Current-voltage and capacitance-voltage characteristics

IV curves are the most fundamental electrical characterization technique for devices. In this thesis, IV curves have been measured to make a very fast evaluation of damaged devices, to determine the order of magnitude of the dark current in QWIPs and to evaluate the rectification behavior of processed Schottky contacts. IV curves are measured by using a Keithley 617 electrometer, combined with a Keithley 230 voltage source.

In those situations where the residual electron concentration is beyond the detection limit of the Hall effect technique, capacitance-voltage profiles are recorded to assess the electron concentration. To do so, Schottky contacts are processed as described in Section 3.1.2. At the metal-semiconductor interface the Fermi levels are aligned, inducing a band bending at the semiconductor side. Hence, a depletion layer is formed and its width is given by¹¹⁰

$$W_d = \sqrt{\frac{2\varepsilon}{eN}(V_{bi} + V_a)}, \quad (3.8)$$

where ε is the dielectric constant of the depleted material, N is the density of ionized doping centers, V_{bi} is the built-in bias voltage of the junction, and V_a is the externally applied voltage.

From Eq. 3.8 it can be observed that the depletion width can be modulated with the applied voltage. The depletion region of the semiconductor can be considered as a parallel plate capacitor with a known capacitance of

$$C = \frac{\epsilon A}{W_d}, \quad (3.9)$$

where A is the diode area. Then, combining Eqs. 3.8 and 3.9, the capacitance of the junction can be expressed as

$$C = \epsilon A \sqrt{\frac{eN}{2\epsilon(V_{bi} + V_a)}}. \quad (3.10)$$

The capacitance of the junction is measured at each voltage step, and a doping profile of the semiconductor is obtained. For the acquisition of the CV profiles, a Boonton 7200 capacitance meter working at 1 MHz is used.

Part II

Results: ZnO/(Zn,Mg)O heterostructures

Chapter 4. Characterization of (Zn,Mg)O:Ga with high Mg contents and Ga doping levels

The results in this chapter are reproduced from the article “Ga-doping of nonpolar *m*-plane ZnMgO with high Mg contents”, published in the Journal of Alloys and Compounds, 766, 436 (2018), by **J. Tamayo-Arriola**, M. Montes Bajo, N. Le Biavan, D. Lefebvre, A. Kurtz, J.M. Ulloa, M. Hugues, J.-M. Chauveau and A. Hierro.¹¹¹ The results are used in accordance with the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

The results were also presented by the author at the European-Materials Research Society conference, celebrated in Warsaw, Poland, in September 2017.

4.1. Introduction

The interest in modifying the optical and transport properties of ZnO and the understanding of the arising physical phenomena when doing so were briefly described in Chapter 1. The growth of epitaxial ZnO is needed in devices that require a high control over the heterointerface with a (Zn,Mg)O alloy that serves as the barrier, such as high electron mobility transistors (HEMTs)^{112,113} and intersubband based devices,^{114,115} including QWIPs and QCLs. The main characteristic of these devices is that they are unipolar, i.e. they are based on the use of majority charge carriers, so the lack of reliable p-type ZnO¹¹⁶ is not a drawback. Thus, the analysis is focused on the CB of the material, and the CB offset between the ZnO and the (Zn,Mg)O alloy is controlled via the Mg content. Besides, in the case of HEMTs the two-dimensional electron gas (2DEG) density at the interface is tuned through the Ga doping in the (Zn,Mg)O barrier, provided there are no internal electric fields or their effect is negligible.

The aim of this chapter is to study the effects the addition of Mg and Ga atoms has in the wurtzite crystalline structure of ZnO, as well as their interplay, which plays an important role in the material properties especially when high Mg contents and Ga doping levels are achieved. To do so, a combination of Hall effect, IR reflectance spectroscopy, and CV profiling techniques were used for measuring the electron concentration over the range from 10^{15} to $> 10^{19}$ cm⁻³, and UV-VIS absorption spectroscopy was used in order to determine the optical bandgap of the set of samples.

4.1.1. Description of the samples

As discussed in Section 2.1.1, by alloying ZnO with MgO the bandgap can be increased from 3.37 eV to 6.4 eV, corresponding to the bandgap values of ZnO and MgO in the wurtzite phase, respectively. However, the different thermodynamically-stable crystalline structures of ZnO and MgO limit the Mg content achievable before phase segregation, which for the MBE growth technique has been reported to be about 56 %.⁵⁷

The samples analyzed in this chapter were grown by MBE at CNRS, with Mg contents from 0 to 50 % and three different Ga doping levels, as indicated in Figure 4.1. The nominal Mg content of the samples was previously confirmed by energy-dispersive X-ray spectroscopy. The structure of the samples, shown in Figure 4.1, consists of a 0.43 mm-thick sapphire substrate and the 1 μm -thick (Zn,Mg)O:Ga analyzed layer. The MBE system where the samples were grown is equipped with Zn, Mg, and Ga solid source cells, whereas O is provided by a plasma cell operating at 300 W and the O flow is set to 1 sccm.¹¹⁴ The substrate temperature was set to 380 °C.

Figure 4.1. Structure of the samples characterized in this chapter, and Mg contents and Ga doping levels.

The samples were grown on sapphire substrates having also a wurtzite crystalline structure. Both the sapphire substrate and the alloys have *m*-plane orientation, with the *c*-axis lying on the plane of the surface. However, the *c*-axis of the (Zn,Mg)O:Ga films is rotated 90° with respect to the *c*-axis of the sapphire substrate, as indicated in Figure 4.1.¹¹⁷ The *m*-plane non-polar crystalline orientation is chosen to avoid internal electric fields in the growth direction, which in the case of intersubband-based devices leads to undesired effects that degrade the performance, such as the quantum confined Stark effect.⁸⁸ Also, this orientation would allow to control the 2DEG in HEMTs through the Ga doping in the barrier, avoiding the influence of the electric field on the electron population.

4.2. Infrared reflectance spectroscopy

Measuring the samples with the FTIR spectrometer in the reflection configuration (see Section 3.2.2) is a powerful tool to assess some basic parameters of the dielectric function of the material, such as the plasma frequency, the phonon modes, and the high-frequency dielectric constant. These parameters shape the reflectance spectra in the mid-IR and provide useful information about the behavior of the free electrons and lattice vibrations. First, the reflectance spectra are measured and then fitted by applying a dielectric function model. All the reflectance spectra in this thesis were fitted with a commercial package which applies the transfer matrix method (TMM) to obtain the reflectance of a layered system, where the dielectric function of each layer is previously defined.

4.2.1. Measurement geometry

The LO collective excitations of the material occur at the frequencies where the dielectric function vanishes, and the energy loss function has a maximum. Since the electromagnetic waves are transverse, with the electric field (and so the magnetic field) perpendicular to the direction of propagation of the wave, they cannot couple to LO modes in an infinite medium, whose dipoles are parallel to the direction of propagation. However, in the vicinity of an interface between two media, the symmetry is broken in the direction normal to the interface and, if light is *p*-polarized, LO oscillations are excited, producing a sharp minimum in the reflectance spectra. Thus, most of the analysis done in this and subsequent chapters regarding IR reflectance spectroscopy is restricted to *p*-polarization, while *s*-polarization is used for a double-check of the fitted parameters. For more details about the origin of the minimum observed in the reflectance spectra see Appendix B.

Due to the crystal anisotropy, both sapphire and the (Zn,Mg)O:Ga alloy have axial and planar phonon modes, from now on represented with letters *A* and *E*, respectively. In the *A* modes, the atomic displacement is parallel to the *c*-axis, whereas in the *E* modes it is perpendicular. In order to excite *A* or *E* modes, the electric field must have the same direction as the atomic displacement.

When the *m*-plane (Zn,Mg)O:Ga layers are grown in *m*-plane sapphire, an extra difficulty for analyzing and fitting the reflectance spectra arises. The *c*-axis of (Zn,Mg)O:Ga is rotated 90° with respect to that of sapphire, so in *p*-polarization is not possible to excite separately the *A* or the *E* modes of both (Zn,Mg)O:Ga and sapphire. Since the interest of

the study is to analyze the optical and electrical properties of the (Zn,Mg)O:Ga layer, the reflectance spectra measured and shown in this chapter are taken with the c -axis of the alloy always perpendicular to the electric field in p -polarization, as in Figure 4.2.

Figure 4.2. Reflectance measuring geometry.

In this orientation, the pure E modes of the alloy and a mix of the E and A modes of the sapphire substrate are excited.

4.2.2. Modelling the reflectance spectra

The TMM allows to compute the transmittance and reflectance of a multilayered system when the dielectric function of each constituent layer is known. The simplest scenario is that of a single interface between two media, as represented in Figure 4.3.

Figure 4.3. Amplitude coefficients of the electric field of an electromagnetic wave impinging, being reflected and refracted at the interface between medium 1 and medium 2.

In Figure 4.3, $E_i^\pm$ (where $i = 1, 2$) stand for the amplitude coefficients of the electric field of an electromagnetic wave propagating in media 1 and 2, described by

$$\mathbf{E}_i(\mathbf{r}) = E_i^+ e^{ik_i^+ \mathbf{r}} + E_i^- e^{ik_i^- \mathbf{r}}, \quad \text{with } i = 1, 2, \quad (4.1)$$

and $\mathbf{k}_i^\pm$ are the wavevectors of the wave in media 1 and 2, defined as

$$\mathbf{k}_i^\pm = k_0 \sqrt{\varepsilon_i(\omega)} (\pm \hat{z} \cos \theta_i + \hat{x} \sin \theta_i), \quad \text{with } i = 1, 2. \quad (4.2)$$

In Eq. 4.2, θ_i is the angle between the normal and the direction of propagation of the wave, and $\varepsilon_i(\omega)$ the dielectric function in each medium.

The $E_i^\pm$ amplitude coefficients at both media are related by a transfer matrix (T^{21}), as

$$\begin{pmatrix} E_2^+ \\ 0 \end{pmatrix} = T^{21} \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} = \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix} \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix}. \quad (4.3)$$

Applying the boundary conditions at the interface ($z = 0$), it can easily be demonstrated that the coefficients of the transfer matrix depend on the modulus of the wavevectors in media 1 and 2,¹¹⁸ as

$$T^{21} = \frac{1}{2k_2} \begin{pmatrix} k_2 + k_1 & k_2 - k_1 \\ k_2 - k_1 & k_2 + k_1 \end{pmatrix}, \quad (4.4)$$

and therefore depend on the dielectric function of both media.

In case more interfaces are added to the system, the overall transfer matrix will be the multiplication of the individual transfer matrices of each interface, as

$$\begin{pmatrix} E_n^+ \\ 0 \end{pmatrix} = T^{21} T^{32} \dots T^{n(n-1)} D \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix}, \quad (4.5)$$

where n stands for the number of interfaces in the system. Note that an extra matrix D has been introduced, which contemplates the phase change of the wave through the thicknesses of the different layers in the system. Therefore, to model the reflectance and transmittance spectra, the dielectric function and thickness of each individual layer must be known. Further details on the application of the TMM can be found in many books and are beyond the scope of this work,^{119,120} since the calculations were performed with a commercial software.

Prior to the application of the TMM the dielectric function of each material must be defined, and has to account for the interaction of the IR light with the lattice structure and the free electrons. Phonons could be represented by simple harmonic oscillators, with a dielectric function in the form of⁹⁷

$$\varepsilon(\omega)_j = \varepsilon_{\infty,j} \prod_{i=1}^{n_j} \frac{\omega_{LO,ij}^2 - \omega^2 - i\omega\gamma_{LO,ij}}{\omega_{TO,ij}^2 - \omega^2 - i\omega\gamma_{TO,ij}}, \quad (4.6)$$

where ε_{∞} is the high-frequency dielectric constant, $\omega_{TO,LO}$ the frequencies of the transversal optical (TO) and longitudinal optical (LO) vibrational modes, and $\gamma_{TO,LO}$ the damping of the TO and LO oscillators. The product runs through the phonon modes (i) with A or E symmetry (j).

Regarding the interaction between light and free electrons, as described in Section 2.5, the Drude model reproduces well the dielectric function

$$\varepsilon(\omega) = -\frac{\omega_p^2}{\omega^2 + i\omega\gamma_p}. \quad (4.7)$$

Thus, in a polar, doped semiconductor, such as the (Zn,Mg)O:Ga ternary, the final dielectric function has oscillators as that in Eq. 4.6 added to Drude oscillator in Eq. 4.7. For frequencies well above the plasma frequency and the reststrahlen bands of the phonon modes, the reflectance spectra of the layer have several Fabry-Perot interference fringes, whose period depend on ε_{∞} and the layer thickness d . Thus, the layer thickness is also used as a fitting parameter.

4.2.3. Phonon modes

The effect of the sapphire substrate on the reflectance spectra is considered by measuring and modelling a reference sapphire substrate: its phonon modes and high-frequency dielectric constant are determined. Sapphire has 4 planar and 2 axial phonon modes. For the two possible orientations of the sapphire substrate shown in Figure 4.4, the reflectance spectra in p -polarization and the corresponding fitted curves are shown in Figure 4.5. Indeed, for measuring and fitting the (Zn,Mg)O:Ga layers the chosen orientation of the sapphire substrate is that of Figure 4.4 (b), with the c -axis of sapphire at 45° with respect to the electric field, which allows to have the c -axis of (Zn,Mg)O:Ga always perpendicular to it.

Figure 4.4. Orientations of the sapphire substrate used for deriving its phonon modes. (a) With the c -axis perpendicular and (b) at 45° respect to the electric field.

When the sapphire c -axis lies perpendicular to the electric field, only the E modes are observed (Figure 4.5 (a)). However, when the substrate is rotated 90° , the electric field has a parallel and a perpendicular component relative to the c -axis, and both A and E modes are excited. As observed, the mix of the reststrahlen bands corresponding to the different phonon modes produces a series of valleys and dips, ending at the more energetic LO mode, i.e. the E_4 (LO). From the fitted curve all modes are derived, listed in Table 4.1, and compared with those previously obtained by Schubert *et al.*¹²¹

Figure 4.5. Reflectance spectra (continuous lines) and fits (dashed lines) in p -polarization at 45° angle of incidence of the bare m -plane sapphire substrate. (a) c -axis perpendicular and (b) at 45° respect to the electric field. The blue arrows indicate the planar phonon modes and the brown arrows the axial phonon modes.

(cm ⁻¹)	Schubert <i>et al.</i> (IR ellipsometry)				This work (IR reflectance)			
	E_i	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}	ω_{TO}	γ_{TO}	ω_{LO}
1	385	3.3	388	3.1	385	3	387	3
2	439	3.1	481	1.9	439	1	480	2
3	569	4.7	629	5.9	570	5	629	5
4	634	5.0	907	14.7	633	6	905	17
A_i								
1	398	5.3	511	1.1	397	5	510	1
2	582	3.0	881	15.4	582	3	881	19

Table 4.1. *m*-plane sapphire planar and axial phonon modes, from Schubert *et al.*¹²¹ (left) and fitted in this work (right).

As observed, the values obtained in this work show an excellent agreement with the values reported by Schubert *et al.*, and they are used as input parameters for modelling the reflectance spectra of the (Zn,Mg)O:Ga layers.

Regarding the (Zn,Mg)O:Ga films, the phonon modes are obtained from the not intentionally doped (nid) series and then used as input parameters for the doped ones, providing an accurate fit not only in the reststrahlen band but also above it. Assessing properly the phonon modes is a prerequisite for evaluating the contribution of the free electrons to the dielectric function of the material. ZnO has two polar modes, one in the *E* symmetry and the other in the *A* symmetry.⁴⁵ Other non-polar and silent modes are beyond the scope of this analysis and are not considered, since they do not alter the reflectance spectra of the films. When Mg is introduced, an extra local mode associated with Mg atoms arises in the *E* symmetry. In Figure 4.6, the reflectance spectra and fits of the nid samples in *p*-polarization and with the electric field perpendicular to the (Zn,Mg)O *c*-axis is shown (corresponding to the orientation shown in Figure 4.2). The fitted phonon modes for each Mg content are summarized in Figure 4.7.

Figure 4.6. Reflectance spectra (continuous lines) and fits (dashed lines) in p -polarization at 45° angle of incidence of the m -plane (Zn,Mg)O layers.

The obtained damping factors range from ~ 10 to 70 cm^{-1} , in agreement with Bundesmann *et al.*⁴⁵ The upper branch of the E_1 (LO) phonon mode and the lower branch of the E_1 (TO) mode show a linear tendency when Mg is incorporated, as in the work from Bundesmann *et al.*,⁴⁵ whereas their complementary branches are invariable with Mg.

Figure 4.7. Phonon mode frequencies with E symmetry for the n-doped (Zn,Mg)O films, obtained by IR reflectance spectroscopy.

4.2.4. Plasma frequency and optical mobility

Once the contribution of lattice vibrations to the dielectric function is known, the contribution of free electrons is studied. Plasma frequencies below $\sim 700 \text{ cm}^{-1}$ yield undetectable changes in the reflectance spectra, setting the lower detection limit for the optical electron concentration and optical mobility that can be determined with this method. The fitted reflectance spectra of the ZnO samples with the three Ga doping levels is shown in Figure 4.8 and the extracted values of the plasma and damping frequencies of all samples are summarized in Table 4.2.

Figure 4.8. Reflectance spectra (continuous lines) and fits (dashed lines) in p -polarization at 45° angle of incidence of the m -plane ZnO:Ga layers.

As observed in the reflectance curves with higher plasma frequencies, there is a minimum at the plasma frequency, and below it, the reflectance values are higher, since the real part of the dielectric function is negative and light cannot propagate within the material. The plasma frequency was previously defined as $\omega_p = (n e^2 / m_e^* \epsilon_0)^{1/2}$ and, if a constant electron effective mass is assumed, a larger plasma frequency indicates a larger free electron concentration. However, in the (Zn,Mg)O alloy m_e^* depends on the Mg content. Its value has been studied theoretically via local density theory,¹²² *ab initio* calculations,¹²³ and applying a semi-empirical tight-binding model,¹²⁴ and the change with Mg concentration ranges from $0.13x$ to $0.27x$, where x is the Mg content. An intermediate value of $0.22x$ is chosen here, equal to that from Ke *et al.*¹²² Thus, combining the plasma frequency results with the electron effective mass, the optical electron concentration is

deduced and shown in Table 4.2. In the discussion section, these values are compared to the electron concentration obtained from the other techniques.

Samples		Fitted parameters		Derived parameters	
Mg content (%)	Ga-doping (cm ⁻³)	ω_p (cm ⁻¹)	γ_p (cm ⁻¹)	n_{opt} (cm ⁻³)	μ_{opt} (cm ² V ⁻¹ s ⁻¹)
0	nid	--	--	--	--
	6×10^{18}	1760	1506	9.7×10^{18}	139
	4×10^{19}	3677	1451	4.2×10^{19}	144
20	nid	--	--	--	--
	6×10^{18}	816	2915	2.1×10^{18}	62
	4×10^{19}	3695	1430	4.3×10^{19}	126
35	nid	--	--	--	--
	6×10^{18}	--	--	--	--
	4×10^{19}	2633	3964	2.2×10^{19}	32
50	nid	--	--	--	--
	6×10^{18}	--	--	--	--
	4×10^{19}	--	--	--	--

Table 4.2. Values of the fitted parameters from IR reflectance spectroscopy (center column) and calculated parameters for each (Zn,Mg)O:Ga sample (right column). In samples with plasma frequencies below the detection limit (~ 700 cm⁻¹) the values could not be obtained.

On the other hand, the damping of the plasma resonance, γ_p , is related to the optical losses when IR light excites the free electron collective oscillations. Therefore, it is related to the optical mobility (μ_{opt}) through

$$\mu_{opt} = \frac{e}{m_e^* c \gamma_p}. \quad (4.8)$$

The calculated optical mobilities are summarized in Table 4.2 and shown in Figure 4.9 together with the Hall mobility results.

4.3. Hall electron concentration and Hall mobility

The samples with higher electron concentration were characterized by Hall effect, and the Hall electron concentration and Hall mobility were determined. The lowest detectable value analyzed by this technique was that from the (Zn,Mg)O:Ga sample with 20 % Mg content and a nominal Ga-doping value of 6×10^{18} cm⁻³, which yielded $n_{Hall} = 3.2 \times 10^{17}$ cm⁻³. The results of the electron concentrations obtained by Hall effect are discussed

together with the results obtained with other techniques in the discussion section of this chapter.

The Hall mobility values are shown in Figure 4.9 (b), and are similar to the previously reported values for (Zn,Mg)O:Ga.^{125,126}

Figure 4.9. (a) Optical and (b) Hall mobilities for the Ga-doped films as a function of the Mg content.

As observed in Figure 4.9, the Hall mobilities are around a factor of five lower than the optical mobilities, since in Hall effect measurements the electrons are highly affected by extended defects. Besides, both the electrical and optical mobilities decrease with the Mg content. This reduction could have two contributions: the increase of the electron effective mass,^{122,123,127} and the increase of impurity scattering with Mg-related defects. The latter seems to be the dominant factor since the increment of the effective mass would produce a decrease in μ_{opt} of only 8 % from 0 to 35 % Mg, much lower than the measured behavior. Besides, it is puzzling that both the electrical and optical mobilities increase with the Ga doping, contrary to what ionized impurity-limited scattering would predict. Considering the model proposed by Seto *et al.*¹²⁸ for polycrystalline films, the traps found between grain boundaries generate a potential barrier whose height has a maximum for a critical doping concentration. As doping is further increased its height is reduced, producing a rise of the electron mobility, as the one observed. In this study, this effect likely originates from the threading dislocations¹²⁹ found when ZnO is grown on sapphire.

4.4. Capacitance-voltage profiling

The samples with electron concentration below the detection limit for Hall effect and reflectance spectroscopy were analyzed by CV profiling. To do so, Schottky diodes were processed, and the depletion region under the semiconductor-metal interface was modulated by a reverse bias. The capacitance of the junction was thus measured as a function of the depletion depth, as described in Section 3.5. From an analysis of $1/C^2$ vs applied bias, the concentration of the ionized impurities was obtained.¹¹⁰ The lower detection limit is set by the conditions on which the depletion region is as wide as the 1 μm depth of the film, corresponding to an electron concentration of $1 \times 10^{15} \text{ cm}^{-3}$. Figure 4.10 shows the derived doping depth profile for the three samples measured by this technique.

Figure 4.10. Electron concentration from CV profiling as a function of the depletion depth.

As observed, in the film with a lower residual concentration (the nid ZnO film) the depletion region was modulated over a wider depth range, while in the samples with electron concentrations around $\sim 1 \times 10^{18} \text{ cm}^{-3}$ the range was restricted to a few nanometers. In films with $n > 1 \times 10^{18} \text{ cm}^{-3}$ the high electron concentration inhibits the depletion layer to be formed, setting the upper detection limit for this technique. The n results obtained with CV profiling are compared with the values from Hall effect and IR reflectance measurements in the discussion section of this chapter.

4.5. Optical bandgap

In addition to the electrical characteristics, the determination of the optical bandgap allows to understand the implications of the concomitant presence of Ga and Mg at high concentrations.

Figure 4.11. (a) Square of the absorption spectra times the energy from the nid samples together with the linear fit used to derive the optical bandgap. (b) Optical bandgap vs Mg content for all samples, where the dashed lines are linear fits. The inset shows the effect of band filling in the ZnO:Ga samples.

Figure 4.11 (a) displays the absorption coefficient of the nid samples, from where the optical bandgap was obtained for each alloy by fitting it in a Tauc plot as a direct optical transition. As expected, the (Zn,Mg)O optical bandgap increases with the Mg content. This technique probes the excitonic bandgap of the alloy rather than the real bandgap, and therefore the change in the exciton binding energy from 60 meV of ZnO to 74 meV for 50 % Mg should be considered.⁸⁷ By doing so, an increment of the bandgap for the nid series of 22.2 meV per Mg percentage is obtained, close to the reported values of 23 – 25 meV / %.^{84,87}

On the other hand, for the ZnO films, there is a clear blue-shift of the optical bandgap with increasing Ga content (inset of Figure 4.11 (b)) of up to 32 meV. Indeed, increasing the electron concentration moves the Fermi level above the CB minimum, resulting in the Burstein-Moss shift (E_{BM}).⁶⁴ However, for large donor and electron concentrations, a bandgap shrinkage is also present (E_{SH}), produced by the merging of the donor miniband with the CB,¹²⁷ and by the bandgap renormalization, which is due to many-body effects such as electron-electron and electron-impurity interactions.⁵⁰ Therefore, the total change in the optical bandgap (ΔE_g^{opt}) is given by the two contributions, as

$$\Delta E_g^{opt} = E_{BM} - E_{SH}. \quad (4.9)$$

The Burstein-Moss shift was given by Eq. 3.3, where the electron effective mass depends on the CB non-parabolicity, as

$$m_e^* = m_{e,CBM}^* \left[1 + 2\alpha_{np} \frac{\hbar^2}{m_{e,CBM}^*} (3\pi^2 n)^{\frac{2}{3}} \right]^{\frac{1}{2}}, \quad (4.10)$$

and $m_{e,CBM}^*$ is the electron effective mass as the CB minimum ($m_{e,CBM}^* = 0.28 m_0$).⁴⁷ The non-parabolicity factor was taken to be $\alpha_{np} = 0.33 \text{ eV}^{-1}$.¹³⁰ The optical electron concentration was assumed to be equal to n (indeed they are equal, as discussed in Section 4.6). The obtained E_{BM} is 149 meV for the ZnO film where $n = 4.5 \times 10^{19} \text{ cm}^{-3}$. This shift is considerably larger than the one obtained experimentally of 32 meV, so the difference is attributed to E_{SH} . In addition, in the Mg-containing films, a red-shift is observed in the optical bandgap as the Ga doping is increased, suggesting that the effects causing bandgap shrinkage have more impact than band filling.

Looking at the absorption spectra, it is also evident that as the Mg content is increased there appears an exponential Urbach tail below the band-edge energy,¹³¹ effect that is more prominent for higher Mg contents. This tail originates from the presence of defect-related energy states within the bandgap. In order to quantify it, the absorption coefficient was fitted in the vicinity optical bandgap absorption, with the Urbach equation

$$\alpha(E) = \alpha_0 \cdot e^{\frac{E - E_g^{opt}}{E_u}}, \quad (4.11)$$

where α_0 is a constant and E_u is the Urbach tail energy.

Figure 4.12. (a) Urbach fit of the absorption coefficient for nid (Zn,Mg)O films, and (b) extracted Urbach tail energies for all samples.

As shown in Figure 4.12, the Urbach tail increases strongly with the Mg content, from 45 to 105 meV, but it is rather insensitive to Ga doping. Thus, the presence of Mg-related impurities is likely at its origin.

4.6. Discussion

To have a complete view of the role that Mg and Ga have in the crystalline structure and the potential physical origin of the effects they produce, all the results need to be considered.

Figure 4.13 shows the electron concentration obtained from all techniques and a clear compensation related to the incorporation of Mg is observed. The ZnO nid sample shows a residual electron concentration of $9 \times 10^{16} \text{ cm}^{-3}$ from CV profiling, somehow higher than the reported values for ZnO grown on native *m*-plane ZnO substrates,⁴⁸ whereas the rest of the nid samples are fully depleted, so their electron concentration is below $1 \times 10^{15} \text{ cm}^{-3}$. In fact, looking at the drop in electron concentration between the ZnO:Ga sample and the (Zn,Mg)O:Ga alloy with 20 % Mg and a Ga doping of $6 \times 10^{18} \text{ cm}^{-3}$, it is deduced that as a

result of adding Mg there is a drop in the electron concentration of as much as $6 \times 10^{18} \text{ cm}^{-3}$, effect that is negligible for the highly doped samples, where the Ga doping is $4 \times 10^{19} \text{ cm}^{-3}$. Thus, for the lowest doping level, the drop of the electron concentration starts at lower Mg contents, while it is possible to maintain high electron concentrations in samples with high nominal Ga-doping levels even for high Mg contents. This implies that doping efficiencies close to 100 % are achieved for alloys with Mg contents up to 35 %, with $n_{opt} \sim 4.4 \times 10^{19} \text{ cm}^{-3}$, matching quite well the nominal doping level.

Figure 4.13. Extracted electron concentration as a function of Mg, for different Ga doping levels. The symbol type indicates the technique employed, and the colors the Ga doping level. The red shaded area indicates the electron concentration range beyond the detection limit for all techniques. The data points within this shaded area correspond to samples fully depleted where the electron concentration could not be extracted.

The electron compensation is also noticeable when the electron concentration is calculated in the same film with different techniques. The differences that arise in a given sample by using different techniques are related to the physical mechanisms driving the experimental observations. With reflectance spectroscopy local oscillations of the free electrons are excited, and the optical electron concentration is determined locally, in contrast to Hall effect where the electrons travel microscopically and are heavily affected by extended defects. Thus, in the five films where both Hall and IR reflectance

measurements were performed, n_{opt} is always equal to or larger than n_{Hall} , allowing us to confirm the high doping efficiencies discussed above. In the case of CV profiling, the static charge is measured, and both the ionized donors and the defects acting as electron traps contribute to the measured electron concentration provided the electron emission time constant is comparable to that from the probing frequency. Therefore, CV profiling also yields electron concentrations closer to the layer doping concentration than Hall effect. In the only film where n could be measured by all three techniques (i.e. the film with 20 % Mg nominally Ga-doped to $6 \times 10^{18} \text{ cm}^{-3}$), results from CV profiling and reflectance match well, with $n \sim 1.0 \times 10^{18} \text{ cm}^{-3}$. However, from Hall effect a significantly lower value of $n_{Hall} = 3.2 \times 10^{17} \text{ cm}^{-3}$ is obtained, and the drop is attributed to the trapped electrons at the energy levels close to the CB minimum responding to the modulated signal in CV profiling. On the other hand, this value is lower than that for the ZnO sample with equal nominal doping, and the drop is thus assigned to the formation of acceptor-like deep levels.

The origin of the electrical compensation could be attributed to different factors on which Mg and/or Ga are involved. The major one is the formation of intrinsic zinc vacancies (V_{Zn}), which are responsible for deep levels close to the valence band of ZnO.¹³²

Several studies point at V_{Zn} as the dominant compensating acceptor in n-type ZnO,^{133,134} especially when the films are grown under O-rich conditions, and some of them suggest the incorporation of Mg favors the presence of these acceptors.^{135,136} The formation energy of V_{Zn} decreases as the Fermi level approaches the CB minimum,¹³⁷ so that the density of V_{Zn} acceptors should increase also with the Ga content.¹³⁴ Moreover, there could also be some other defect complexes forming, such as Ga interstitials (Ga_{Zn}) interacting with V_{Zn} , e.g. the $Ga_{Zn}-V_{Zn}$ acceptor pairs. Indeed, Demchenko *et al.*¹³⁷ computed the formation energy for $Ga_{Zn}-V_{Zn}$ complexes in ZnO and found it to be even lower than the formation of V_{Zn} when growing under O-rich conditions. It is also interesting to point out that as a consequence of the high doping efficiencies observed for the films with Mg contents up to 35 %, it is unlikely that the increase in the effective mass with the Mg content has an impact on the donor efficiency, as considered by Lu *et al.*,¹²⁷ where the hydrogenic donor model was assumed.

Concerning the optical bandgap, the blue-shift observed in Figure 4.11 (b) for the ZnO films comes from the band filling, which dominates over the bandgap shrinkage. However, this effect is not observable in the films with Mg, where a red-shift occurs. This shift likely

originates from the semiconductor-metal transition: when the donor concentration exceeds the critical concentration (n_c) at which the transition is expected to occur in ZnO, in the range of $n_c \sim 2 \times 10^{18} - 2 \times 10^{19} \text{ cm}^{-3}$,¹²⁷ a bandgap reduction should be evident at $n \approx 1$ to $10 n_c$ due to the merging of the donor and conduction bands. Bandgap renormalization is discarded since it plays a role only when high electron concentrations are present, and a red-shift is observed even in fully depleted samples.

4.7. Conclusion

From the combination of CV profiling, Hall effect, IR reflectance and UV-VIS absorption spectroscopy the effect that Ga doping has on the transport and optical characteristics of non-polar *m*-plane (Zn,Mg)O alloys was analyzed. Here it is shown that by using MBE growth, the wurtzite phase can be maintained up to 50 % Mg contents, where the optical bandgap reaches $\sim 4.41 \text{ eV}$. Also, the employment of different techniques for assessing the electron concentration allows to confirm that Ga-doping efficiencies close to 100 % can be achieved for Mg contents in the alloys up to 35 % Mg.

However, the incorporation of large Mg contents involves a clear degradation of the electrical properties, with a pronounced drop of the electron concentration and mobility. While the mobility decreases likely due to Mg-related impurity scattering, the presence of extended defects, like threading dislocations, produces an unusual increase in the mobility with increasing electron concentration or Ga doping. This effect is due to the lowering of the Coulomb potential barrier formed around the extended defects. The results also suggest that the physical origin of the electrical compensation lies mainly in the deterioration of the crystal quality of the (Zn,Mg)O:Ga alloys, with the formation of extended defects, and the emergence of $\text{Ga}_{\text{Zn}}\text{-V}_{\text{Zn}}$ acceptor complex pairs that increase with the Ga content. Consequently, an increment of the Urbach tail is observed in the absorption spectra for increasing Mg content, from 45 to 110 meV, which is independent of Ga doping level. Besides, although in ZnO:Ga a band filling effect has been observed, for (Zn,Mg)O:Ga alloys a red-shift of the optical bandgap occurs, which is attributed mainly to the merging of donor and conduction bands.

Chapter 5. Intersubband transitions in ZnO:Ga/(Zn,Mg)O multiple quantum wells

The results in this chapter were previously published in the following scientific articles:

- “Multisubband plasmons in Doped ZnO Quantum Wells”, published in the Physical Review Applied journal, 10, 24005 (2018), by M. Montes Bajo, **J. Tamayo-Arriola**, M. Hugues, J. M. Ulloa, N. Le Biavan, R. Peretti, F. H. Julien, J. Faist, J.-M. Chauveau, and A. Hierro.¹¹⁵
- “Homoepitaxy of non-polar ZnO/(Zn,Mg)O multi-quantum wells: From a precise growth control to the observation of intersubband transitions”, published in the Applied Physics Letters journal, 111, 231902 (2017), by N. Le Biavan, M. Hugues, M. Montes Bajo, **J. Tamayo-Arriola**, A. Jollivet, D. Lefebvre, Y. Cordier, B. Vinter F.-H Julien, A. Hierro, and J.-M. Chauveau.¹¹⁴

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5.1. Introduction

This chapter aims to be the continuation of Chapter 4, where the optical and electrical results are used for the design, characterization, and modelling of samples for detecting ISBTs and developing QWIPs.

The ISBTs here explored occur in the conduction band of ZnO:Ga/(Zn,Mg)O heterostructures. ISBTs have already been studied in ZnO-based heterostructures with a polar orientation.^{85,86} Recall that in such orientation the internal electric field can lead to the quantum confined Stark effect.⁸⁸ However, here the heterostructures are non-polar, thanks to the availability of non-polar *m*-plane native ZnO substrates, which offers an alternative to avoid such undesired effects. Besides, the defect density in heterostructures grown homoepitaxially is expected to be lower, with a residual electron concentration as low as $1 \times 10^{14} \text{ cm}^{-3}$.⁴⁸

5.2. Modelling

The modelling of the optical response of the multiple quantum well heterostructures consists of several calculations. Although here the modelling is presented in three different

parts, they are not independent of each other and typically a feedback of the fitted parameters was performed.

5.2.1. Computing the frequency of the intersubband transitions

Following the formalism described in Section 2.4, the frequency of the ISBTs depends on the QW thickness (L_{QW}), on its Ga-doping level, on the electron effective mass, and on the CB offset between the QW and the barrier (i.e. on the Mg content in the barrier). Thus, in order to have ISBTs falling in the mid-IR range of the electromagnetic spectrum, a proper design of the heterostructures is required.

To do so, first the CB profile and the energy levels in a QW are calculated by solving self-consistently the Schrödinger and Poisson equations, and this calculation is carried out with the Aestimo solver.¹³⁸ Since the potential profile depends on the distribution of electrons and ionized donors and *vice versa*, first the Poisson's equation is solved, from where the potential profile is derived, and then introduced in the Schrödinger equation to compute the wavefunctions. This closed-loop is repeated until the solution converges, and the obtained wavefunctions are simultaneously solutions of both Schrödinger and Poisson's equations. To get the solutions, the solver applies the effective mass and the envelope function approximations and the non-parabolicity of the subbands within the QW has been neglected, i.e. the effective mass in the QW was assumed to be k -independent.

The Aestimo solver employs the numerical shooting method to assess the wavefunctions: known the wavefunction at two points $\phi(z)$ and $\phi(z - \delta z)$, where z is the direction perpendicular to the QW planes and δz is a small step length along it, its value at $z + \delta z$ can be derived at a given energy E by expanding its second-order derivative in terms of finite differences, as¹³⁹

$$\phi(z + \delta z) = \left[\frac{2m(z)^*}{\hbar^2} (\delta z)^2 (V(z) - E) + 2 \right] \phi(z) - \phi(z - \delta z). \quad (5.1)$$

Depending on the parity of the energy level and applying the boundary conditions, the two initial values for the wavefunction are set. The energy E_n of the corresponding n^{th} confined level remains an unknown parameter, and it is found with the Newton-Raphson iterative method: the energy E is varied systematically until the wavefunction converges, with $\phi(E_n, z \rightarrow \infty) = 0$.

Further details of the method the Aestimo solver uses to give the required output parameters can be found in the textbook “Quantum wells, wires and dots”, by Harrison and Valavanis,¹³⁹ on which the code is based.

The input physical parameters of the QWs and the barriers used for the calculations are the following:

- The electron effective mass in the barrier was assumed to be $0.28 m_0$,⁴⁷ equal to that in the QW.
- The room temperature bandgap of ZnO is 3.37 eV.¹² The bandgap of the (Zn,Mg)O barrier is assumed to increase with respect to that of ZnO at a ratio of 25 meV per % of Mg, as in Neumann *et al.*⁸⁷
- The CB offset is assumed to be $0.675 \Delta E_g$, where ΔE_g is the difference of the bandgaps of ZnO and (Zn,Mg)O. The values in the literature range from $0.6 \Delta E_g$ to $0.70 \Delta E_g$.^{84–86}

In addition to the CB potential profile, the energy levels in the QW and their corresponding electron wavefunctions, the Aestimo solver gives the oscillator strength of the transitions, the Fermi energy, and the effective width over which the ISBT takes place, which is not necessarily equal to L_{QW} . This effective width is defined as

$$L_{eff,j} = \frac{\hbar}{2S_{j,j+1} m_e^* \omega_{ISBT,j}}, \quad (5.2)$$

where $\omega_{ISBT,j}$ is the frequency of the j^{th} ISBT and

$$S_{j,j+1} = \int_0^\infty \Phi_j(z) \Phi_{j+1}(z) \int_0^z \int_0^{z'} \Phi_j(z'') \Phi_{j+1}(z'') dz'' dz' dz, \quad (5.3)$$

and $\Phi_j(z)$ and $\Phi_{j+1}(z)$ are the electron wave functions corresponding to the levels involved in the ISBT.^{90,140}

5.2.2. Modelling the reflectance of the intersubband transitions

The IR reflectance spectroscopy is not only useful to derive the fundamental optical parameters of the materials, as described in Section 4.2, but also to model the ISBTs. In the heterostructures here analyzed the reflectance measurements are done with the electric field of the incident light perpendicular to the c -axis of the wurtzite structure.

Therefore, the dielectric function of the (Zn,Mg)O barriers can be considered to be isotropic, with the term which accounts for the phonons, as

$$\varepsilon^{(Zn,Mg)O}(\omega) = \varepsilon_{\infty}^{(Zn,Mg)O} \prod_i \frac{\omega_{LO,i}^2 - \omega^2 - i\omega\gamma_{LO,i}}{\omega_{TO,i}^2 - \omega^2 - i\omega\gamma_{TO,i}}, \quad (5.4)$$

where the product runs for the two planar phonon modes of (Zn,Mg)O. However, in the QWs the ISBT is excited only by the component of the electric field transversal to the QW planes, and therefore the dielectric function is anisotropic. The in-plane component accounts for the phonons and plasmons, and the out-of-plane component accounts for the same phonons and for an oscillator term which reproduces the interaction of the light with the ISBTs. Thus, the two components of the dielectric function of the QWs are

$$\varepsilon_{out-of-plane}^{ZnO}(\omega) = \varepsilon_{\infty}^{ZnO} \frac{\omega_{LO}^2 - \omega^2 - i\omega\gamma_{LO}}{\omega_{TO}^2 - \omega^2 - i\omega\gamma_{TO}} - \sum_j \frac{f_j \omega_{p_{2D,j}}^2}{\omega^2 - \omega_{ISB,j}^2 + i\omega\gamma_{ISB,j}} \quad (5.5.a)$$

$$\varepsilon_{in-plane}^{ZnO}(\omega) = \varepsilon_{\infty}^{ZnO} \frac{\omega_{LO}^2 - \omega^2 - i\omega\gamma_{LO}}{\omega_{TO}^2 - \omega^2 - i\omega\gamma_{TO}} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_p}. \quad (5.5.b)$$

In Eq. 5.5.a, the sum in j extends to the number of allowed ISBTs and f_j is the oscillator strength of the j^{th} ISBT. Besides, the damping of the intersubband transition, γ_{ISB} , is extracted from the full width at half maximum (FWHM) of the absorption peak observed in transmittance measurements. The anisotropy is used in order to calculate the electron concentration within the QW, by measuring reflectance in s -polarization and fitting the plasma frequency with the Drude term in Eq. 5.5.b. The obtained values for the electron concentration in the QWs are about a 10 % higher than the nominal values and are employed as input parameters for calculating the QW profile and Fermi energy discussed in the previous section.

At this point, it is worth to remark a subtle difference in the definition of the plasma frequency for the j^{th} ISBT, $\omega_{p_{2D,j}}$, with respect to that of a bulk material, ω_p . The oscillation of electrons in the direction transversal to the QW planes is restricted to $L_{eff,j}$ and the plasma frequency of the j^{th} ISBT in a QW is redefined as

$$\omega_{p_{2D,j}} = \sqrt{\frac{\Delta n_{2D,j} e^2}{L_{eff,j} m_e^* \epsilon_0}} \quad (5.6)$$

where $\Delta n_{2D,j}$ is the difference in the 2D electron density between the j and $j+1$ levels involved in the ISBT. It is related to the plasma frequency given in Eq. 2.17 for the bulk material by

$$\omega_{p_{2D,j}} = \omega_p \sqrt{\frac{\Delta n_{2D,j}}{n_{3D}} \frac{1}{L_{eff,j}}} \quad (5.7)$$

5.2.3. Assessing the intersubband absorption spectrum

Once the modelling described above has been performed and the dielectric function is known, it is straightforward to assess the absorption spectrum of the heterostructure. The derivation of the expression for the absorption coefficient can be found elsewhere,¹⁴¹ and gives the following dispersion relation

$$\alpha(\omega) = -Im \left[\frac{\epsilon_\infty}{\epsilon_{out-of-plane}} \right] n_b \frac{\omega \sin^2 \theta}{c \cos \theta}, \quad (5.8)$$

where n_b is the background, frequency-independent refractive index and θ the angle of incidence.

5.3. Results

The effect of two different parameters on the frequency of the ISBT is evaluated: the thickness of the QW and its Ga-doping level. The Mg content in the barrier is 30 % in every sample, enough to allow several energy levels to be formed and not as high as to have plastic relaxation in the heterostructure. The (Zn,Mg)O barrier thickness in the different samples ranges from 5 to 15 nm, which ensures to have decoupled QWs, and the number of periods is between 10 and 20. In Figure 5.1, a schematic of the heterostructure of the samples and the QW width and Ga doping level of each sample is shown.

Figure 5.1. (Left) Schematic of the heterostructures analyzed in this work. (Right) Details of the quantum well thickness and doping level for each analyzed sample. Two series are distinguished, series A with varying quantum well thickness, shaded in green, and series C with varying QW doping, shaded in blue. Sample B belongs to both series.

A total of 8 samples are characterized, classified in two series: series A, with a fixed Ga doping level and varying L_{QW} , and series C, with very small variations of L_{QW} and varying Ga doping level. Sample B belongs to both series. The minimum doping level was set to $1 \times 10^{19} \text{ cm}^{-3}$, since for lower values the observation of ISBTs by means of IR reflectance and transmittance measurements is not possible. Sample C4 is used as a reference undoped sample for the IR reflectance measurements and simulations.

5.3.1. Effect of the quantum well thickness on the intersubband transition

In this section, the results of series A, in which the QW thickness is varied, are presented. The potential profile and energy levels (e_1 and e_2) for a QW thickness of 3.2 nm, corresponding to sample A3, are shown in Figure 5.2. As observed, there are two confined levels in the QW, separated in energy by 230 meV (1855 cm^{-1}), and the CB offset is about 506 meV (4081 cm^{-1}). The Fermi energy is, for a doping of $1 \times 10^{19} \text{ cm}^{-3}$, above the first confined level and therefore the number of available electrons to be excited is expected to be large enough to visualize the ISBT in the transmittance measurements. Sample A2, with 2.7 nm, has also two confined levels but separated in energy by a larger amount of 280 meV (2258 cm^{-1}). Sample B has three confined levels, but, since the Fermi energy is far from the second level, the absorption strength of the e_2 to e_3 transition is low and a single e_1 to e_2 transition needs to be considered. In contrast, sample A1 features a unique confined level, and no ISBT is expected.

Figure 5.2. Potential profile of a 3.2-nm-wide QW, computed with the Schrödinger and Poisson equations solved self-consistently. The wavefunctions of the two confined levels, e_1 and e_2 , as well as the Fermi energy, E_f , are represented.

The prediction of the model is in good agreement with the transmittance measurements performed in the 45° -polished multipass waveguides. The dimensions of the waveguides will determine the number of passes of the IR light through the active region, and that would affect the strength of the absorption peak observable in the transmittance spectra. For the transmission experiments, the optimized dimensions of the waveguides are between 5 and 6 mm-long, 3 mm-wide, and $500\ \mu\text{m}$ -thick, as indicated in Figure 5.3. That assures about 5 – 6 reflections in the top layer of the active region.

Figure 5.3. Dimensions of the multipass waveguides polished for transmittance measurements. Not to scale.

Some attempts were made also with thinner ($\sim 200 \mu\text{m}$) and longer ($\sim 8 \text{ mm}$) waveguides, in order to increase the number passes through the active region, but the strength of the absorption peak was similar, with the disadvantage of having a much more fragile sample. The factor that most influences the strength of the absorption peak in the transmittance spectra was observed to be the doping level in the ZnO quantum wells, as mentioned in the next section.

In Figure 5.4 (a) the transmittance in s - and p - polarizations is shown, and, in order to clearly determine the position of the absorption peak, the s - to p - transmittance ratio is calculated and shown in Figure 5.4 (b). The ISBT yields a drop of transmittance in p -polarization in the samples with QW thicknesses of 3.7 nm, 3.2 and 2.7 nm, satisfying the ISB selection rules. Those ISBTs correspond to the transition from the ground level to the first level, and, as expected, for a smaller QW thickness the levels are more separated in energy and the ISBT becomes more energetic. This can be clearly seen in the transmittance ratios shown in Figure 5.4 (b), where the frequency falls at 2150, 2400, and 2740 cm^{-1} , in samples with QW thicknesses of 3.7, 3.2, and 2.7 nm, respectively. In contrast, sample A1 has a QW thickness of 2.2 nm and any ISBT is observed, likely due to the existence of a unique confined level within the QW.

Figure 5.4. (a) Transmittance measurements in s - (dotted) and p -polarizations (solid) of the incident light, for the samples corresponding to series A, offset for clarity. In each case, the ISBT is marked with an arrow. (b) Corresponding s - to p - polarization transmittance ratio, offset for clarity.

The measured frequency of the ISBTs is compared with that obtained from the absorption coefficient in Eq. 5.8, and shown in Figure 5.5. As observed, the agreement between the experimental results and the full model is excellent and demonstrates the importance of considering the depolarization shift on the final calculated frequency.

Figure 5.5. Measured frequencies of the ISBT in samples A2, A3, and B (blue symbols), calculated frequencies with the Schrödinger and Poisson equations solved self-consistently (red symbols) and accounting for the depolarization shift (green symbols).

5.3.2. Effect of the quantum well doping on the intersubband transition: multisubband plasmons

In this section, the ISBT results for the series with varying Ga-doping level are shown, corresponding to series C. In those samples, the QW thickness is between 3.7 and 4 nm, however, the main factor which introduces variations in the measured ISB absorption peak is the doping level in the quantum well.

In contrast to the samples with lower L_{QW} , in series C three confined levels are formed. This implies a difference in the treatment of the ISBTs, since there are two allowed transitions: from e_1 to e_2 (with a frequency ω_{12}) and from e_2 to e_3 (with a frequency ω_{23}). The wavefunctions in e_1 and e_3 have the same parity and the ISBT between these two levels is forbidden (see Section 2.4.3). From the calculations, the obtained ω_{12} values are between 1220 and 1560 cm^{-1} and the ω_{23} values being more energetic, from 1810 to 1910 cm^{-1} . Regarding the oscillator strength, the values are very similar in all samples,

between 0.97 and 0.98 for the e_1 - e_2 transition, and between 1.92 and 1.97 for the e_2 - e_3 transition. The potential profile of sample C3 is shown in Figure 5.6. As observed, the Fermi energy in all samples lies above e_1 and increases with the doping level, and in sample C3 it even exceeds e_2 .

Figure 5.6. Potential profile of sample C3, computed with the Schrödinger and Poisson equations solved self-consistently. The wavefunctions of the three confined levels are shown, and the Fermi energies of the samples belonging to series C are marked with the green-dashed lines.

At this point, a modification in the modelling must be done, since the two available electronic transitions cannot be separately considered. The two electronic transitions are coupled by the dipole-dipole Coulomb interaction, and although they have different frequencies, they finally result in a unique collective mode with its own frequency, so known as the multisubband plasmon (MSP).¹⁴² Therefore, the term accounting for the ISBTs in the out-of-plane component of the dielectric function is rewritten to a single harmonic oscillator, as

$$\sum_j \frac{f_j \omega_{p2D,j}^2}{\omega^2 - \omega_{ISB,j}^2 + i\omega\gamma_{ISB,j}} \Rightarrow \frac{f_{MSP} \Omega_p^2}{\omega^2 - \Omega_{MSP}^2 + i\omega\Gamma_{ISB}}. \quad (5.9)$$

In Eq. 5.9, f_{MSP} is the oscillator strength of the MSP, Ω_{MSP} is the effective frequency of the MSP and can be written as the harmonic mean of the ISBTs weighted by their respective plasma frequencies,

$$\Omega_{MSP}^2 = \frac{\sum_i \omega_{p_{2D,j}}^2}{\sum_j \omega_{p_{2D,j}}^2 / \omega_{ISB,j}^2}. \quad (5.10)$$

Moreover, Ω_p is the effective plasma frequency of the MSP, which can be written as the sum of the plasma frequencies of the individual ISBTs:

$$\Omega_p^2 = \sum_j \omega_{p_{2D,j}}^2 = \sum_j \frac{\Delta n_{2D,j} e^2}{L_{eff,j} m_e^* \epsilon_0} \equiv \frac{\Delta n_{2D} e^2}{L_{eff}^{MSP} m_e^* \epsilon_0}. \quad (5.11)$$

From Eq. 5.11, the width where the effective MSP takes place, L_{eff}^{MSP} , can be obtained, assuming $\Delta n_{2D} \approx n_{2D}$,

$$\frac{1}{L_{eff}^{MSP}} = \sum_j \frac{\Delta n_{2D,j}}{n_{2D}} \frac{1}{L_{eff,j}}. \quad (5.12)$$

Considering the MSP approach described above, now the analysis of the IR reflectance and transmittance measurements can be better discussed. First, from the undoped reference sample (C4), the phonon modes and the high-frequency dielectric constant of the n-doped ZnO QWs and (Zn,Mg)O barriers are extracted, since the reststrahlen bands formed by the phonon modes can be better fitted without the contribution of the light-electron interactions. The values are shown in Table 5.1 and used as input parameters for the doped samples.

Phonon modes (in cm^{-1})				
ZnO	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}
E_1	409	11	590	11
(Zn,Mg)O (30 % Mg)				
E_1	418	17	504	60
E_2	531	21	663	18

Table 5.1. Planar phonon modes of ZnO and (Zn,Mg)O (with 30 % Mg) obtained from the fits of the reflectance spectra of the reference sample.

The fitted phonon mode frequencies vary slightly with respect to those of Chapter 4 for the (Zn,Mg)O alloy with 35 % Mg. However, here the Mg content is 30 % and the heterostructures are grown homoepitaxially, and it may introduce the small deviations. The high-frequency dielectric constants of ZnO and (Zn,Mg)O were also determined from the reference sample, being 3.69 and 3.32, respectively.

Once the phonon modes are derived from the reference sample, the rest of the samples are analyzed. In Figure 5.7, the measured and modelled reflectance curves of samples C2 and C4 in both polarizations of the incident light are shown, to see the effect of the doping of the QWs.

Figure 5.7. Reflectance spectra (continuous lines) and fits (dash-dotted lines) of samples C4 (reference) and C2 at 45° angle of incidence in (a) *s*- and (b) *p*-polarizations of the incident light.

Looking at Figure 5.7 (a), the bump observed at approximately $\sim 1200 \text{ cm}^{-1}$ in the doped sample necessarily comes from the in-plane collective oscillation of the free electrons in the QWs, since the doping is the only difference between the two heterostructures. Thus, from the *s*-polarization spectra, the bulk plasma frequency (second term in Eq. 5.5.b) is fitted and the 2D electron density (n_{2D}) is derived for each sample, and its values are summarized in Table 5.2. As expected, the plasma frequency increases with the QW doping level and so does n_{2D} , which is calculated assuming an electron effective mass of $0.28 m_0$.

Sample	L_{QW} (nm); nominal QW doping (cm^{-3})	ω_p (cm^{-1})	n_{2D} (cm^{-2})
B	3.7; 1×10^{19}	2405	0.5×10^{13}
C1	3.7; 2×10^{19}	3302	1.0×10^{13}
C2	4.0; 6×10^{19}	4269	2.2×10^{13}
C3	3.8; 1×10^{20}	7205	4.0×10^{13}

Table 5.2. Plasma frequency and n_{2D} of the studied samples, derived from the fits of the reflectance spectra in s-polarization.

On the other hand, in p -polarization (Figure 5.7 (b)) an additional feature appears at $\sim 2680 \text{ cm}^{-1}$ corresponding to the excited multisubband plasmon, which satisfies the polarization selection rule. To compare it with that of the other samples, the reflectance measurements and fits in p -polarization are shown in Figure 5.8.

Figure 5.8. Reflectance spectra (continuous lines) and fits (dash-dotted lines) of series C, at 45° angle of incidence in p -polarization. (a) View of the reststrahlen band, offset for clarity. (b) View of the region of interest for the multisubband plasmon, offset for clarity. The arrows indicate the presence of the multisubband plasmon. The legend shows the values of n_{2D} extracted from the reflectance fits in s-polarization.

As observed in Figure 5.8 (a), the reststrahlen bands produced by the (Zn,Mg)O and ZnO phonon modes are excellently reproduced with the harmonic oscillators in Eqs. 5.4

and 5.5.a and the values in Table 5.1, not only for the reference sample but also for the samples with doped QWs. The valley observed at $\sim 525 \text{ cm}^{-1}$ is produced by the overlapping of the reststrahlen bands of ZnO and (Zn,Mg)O.

Regarding Figure 5.8 (b), the evolution of the MSP frequency as a function of the doping level in the p -polarized reflectance curves can be observed. Although ω_{12} and ω_{23} values are very similar in all samples, the dip arising from the MSP shifts to higher frequencies as the QW doping is increased, due to the depolarization shift. Besides, its strength also increases with the doping: in the lower-doped samples the effect of the MSP is almost negligible by means of IR reflectance spectroscopy. Therefore, in order to properly determine the frequencies of the MSPs in all samples, transmittance measurements are carried out in the waveguides. The spectra are shown in Figure 5.9.

Figure 5.9. (a) Transmittance spectra of sample C2 in p - and s - polarizations of the incident light, derived from transmittance measurements. (b) s - to p - transmittance ratio of series C. The arrows indicate the frequency of the MSP.

As observed in Figure 5.9 (a), the MSP induces an absorption peak only visible in p -polarization, which in sample C2 is at $\sim 2710 \text{ cm}^{-1}$. The drop in transmittance observed in both polarizations at lower frequencies results from the absorption and reflection of light by phonons. To have a better sight of the absorption peak, the s - to p -polarization transmittance ratio is calculated in all samples and shown in Figure 5.9 (b). Compared with the peak detected in reflectance (Figure 5.8 (b)), in transmittance the effect is more pronounced and allows to discern the MSP frequency for lower doping levels. In the transmittance ratio spectra an only absorption peak is present, which shifts to higher frequencies as the doping increases, in agreement with the MSP approach. The

frequencies of peaks in Figure 5.9 (b) are the same as those observed in the reflectance spectra of Figure 5.8 (b). Besides, from the FWHM of the peaks in the transmittance ratios is straightforward to experimentally determine the broadening of the MSP, Γ_{MSP} , and then use it for the reflectance modelling. In the samples studied in this section Γ_{MSP} was between 800 and 1100 cm^{-1} , similar to that obtained by Belmoubarik *et al.*⁸⁵ and lower than the values obtained by Zhao *et al.*⁸⁶

Once the required parameters of the dielectric function in Eq. 5.5.a have been obtained from the analysis performed on the reflectance and transmittance spectra and the calculations done with the Aestimo solver, the absorption spectra can be modelled with Eq. 5.8. In Figure 5.10, the ω vs n_{2D} dispersion relation of the MSPs is represented.

Figure 5.10. (Top) Multisubband plasmon ω vs n_{2D} dispersion relation, calculated from Eq. 5.8 for a QW thickness of 3.7 nm. The circular symbols indicate the experimental frequencies of the MSPs extracted from transmittance measurements. The dotted horizontal lines indicate the frequencies of the individual non-depolarized e_1 to e_2 and e_2 to e_3 ISBTs and the dashed white lines the maxima of the absorption spectrum at each n_{2D} . (Bottom) ZnO E_1 (LO) phonon ω vs n_{2D} dispersion relation. The horizontal dashed lines indicate the E_1 (TO) and E_1 (LO) frequencies of the ZnO QWs.

As observed, the experimentally determined MSP frequencies of all samples are in excellent agreement with the calculated ones using the MSP approach. For increasing doping level the depolarization shift becomes the most important factor for the frequency of the MSP: in the samples here analyzed, the doping levels are so high that the MSP frequency lies above ω_{23} , shifting up to 3950 cm^{-1} in sample C3, about three times higher than ω_{12} . Besides, when the Fermi energy exceeds e_2 two resonances are distinguished, as the dashed white lines indicate. For such high Fermi energies, the difference in the 2D electron density between the e_2 and e_3 levels increases and therefore $\omega_{p_{2D}}$ (Eq. 5.6). Thus, the absorption strength of the e_1 - e_2 transition is transferred to that of the e_2 - e_3 transition, in agreement with the theoretical paper by Alpegiani and Andreani.¹⁴³ Also, from the color scale of Figure 5.10, the computed absorption of the MSP increases with n_{2D} , in agreement with the reflectance and transmittance measurements shown in Figure 5.8 (b) and Figure 5.9 (b), where the MSP effect becomes more pronounced for the samples with higher doping levels.

Regarding the bottom graph of Figure 5.10, the phonon and MSP oscillators of the out-of-plane dielectric function are not independent of each other, and their coupling yields the shift of the LO phonon from its original frequency of 590 cm^{-1} to lower frequencies as n_{2D} increases. Thus, the resonance crosses the otherwise prohibited reststrahlen band, established between the E_1 (TO) and E_1 (LO) ZnO phonons. This coupling between the phonons and the electrons involved in the MSP leads to a quasiparticle known as the intersubband polaron.¹⁴⁴ However, in the transmittance experiments the substrate is opaque in the region of interest for examining the polaron, and in the reflectance experiments carried out the polaron was not observed. A plausible explanation is that the large broadening of the MSP ($\sim 800 \text{ cm}^{-1}$) compared to the expected shift of the E_1 (LO) phonon ($\sim 40 \text{ cm}^{-1}$), makes it imperceptible in reflectance experiments.

Finally, in Figure 5.11 the absorption spectra of sample C3 is shown, calculated with three different approaches: a model which treats the ISBTs individually and adds the absorption spectra of both of them, a model with a summation of two ISBT oscillators in the out-of-plane dielectric function (left-hand-side of Eq. 5.9), and a model with the effective MSP oscillator in the out-of-plane dielectric function (right-hand-side of Eq. 5.9).

When the ISBTs are treated individually, the model gives two absorption peaks of similar magnitude. Conversely, if the dielectric function accounts for two oscillators added together, the e_2 - e_3 transition gains strength to the detriment of the e_1 - e_2 transition. In

addition, it appears at a higher frequency than the individually-treated e_2 - e_3 transition, as a consequence of the strong depolarization. Finally, when the approach of the MSP is considered, a single absorption peak appears, resulting from the dipole-dipole interaction of the two individual transitions, in agreement with the experimental results discussed above.

Figure 5.11. Absorption spectra for the two allowed transitions of sample C3, calculated using three different models: two independent ISBTs (blue), a sum of Lorentzian oscillators in the out-of-plane dielectric function (orange), and a single multisubband coupled transition (green). Note the semilogarithmic scale and how the sum of Lorentzian oscillators gives essentially the same results as the MSP approach.

To sum up, in this section of Chapter 5 intersubband transitions have been demonstrated in non-polar homoepitaxial ZnO/(Zn,Mg)O heterostructures. The effect of the QW thickness has been analyzed, with excellent agreement between the modelled and measured ISB frequencies. Besides, in wide QWs (~ 4 nm) the formation of three confined levels has made necessary the implementation of the MSP approach, with the dipole-dipole interaction between the two allowed ISBTs. These results offer perspectives for optoelectronic applications in the mid-IR and THz ranges, based on non-polar ZnO:Ga/(Zn,Mg)O heterostructures.

5.4. Quantum well infrared photodetectors

5.4.1. Samples design and description

The acquired knowledge on the ISBTs is now used in order to design QWIPs operating in the mid-IR. The structures were grown at CNRS with small variations on the QW thickness, on its doping level, and on the Mg content in the barriers. The structure is schematized in Figure 5.12 (a) and the details of the designed samples are shown in Table 5.3.

Figure 5.12. (a) Heterostructure of the samples designed for processing QWIPs. (b) Schematic of the potential profile of a QW with two confined levels.

As observed in Figure 5.12 (b), these samples have two confined levels and the Fermi level lies above e_1 , to keep it populated and e_2 unpopulated and increase the absorption strength.

Sample	L_{QW} (nm)	QW doping (cm^{-3})	Mg content (%)
Q1	2.8	2×10^{19}	20
Q2	3.0	2×10^{19}	20
Q3	2.7	3×10^{19}	30

Table 5.3. Quantum well width, doping level and Mg content of each sample designed for processing QWIPs.

There are three main differences with respect to the previously designed samples for detecting ISBTs:

- In order to have electrical access, 100 and 200 nm-thick Ga-doped ZnO layers were grown at the top and bottom of the multiple quantum well structure, respectively.
- The minimum thickness of the barrier is set to 10 nm, which avoids the overlap of the wavefunctions of adjacent QWs, and thus dark current due to tunneling is minimized.
- The optimum QW thickness is about 3.0 nm, to maintain the first excited level close to the CB minimum in the barrier and increase the escape efficiency of the photo-excited electrons.

In Table 5.4 the following parameters calculated for the design of the QWIPs are shown: the CB offset, the depolarized ISBT ($\tilde{\omega}_{12}$), the escape energy (ΔE), the Fermi energy with respect to e_1 ($E_f - e_1$).

Sample	CB offset (meV)	$\tilde{\omega}_{12}$ (meV)	ΔE (meV)	$E_f - e_1$ (meV)
Q1	338	242	44	74
Q2	338	272	66	83
Q3	506	391	115	65

Table 5.4. Calculated CB offset, depolarized ISBT, escape energy, and Fermi energy with respect to e_1 for each sample designed for processing QWIPs.

5.4.2. Formation of cracks during the wet chemical etching

The processing of QWIPs faced a problem arising during the wet chemical etching with diluted H_3PO_4 (0.1 % in volume): deep grooves were revealed perpendicular to the c -axis of the wurtzite structure, as shown in the Nomarsky microscope pictures of Figure 5.13.

Figure 5.13. Nomarsky top views of a sample designed for processing QWIPs, with the resist patterns corresponding to the first lithography already formed. (a) Before being etched, (b) after 1 minute and (c) after 6:20 minutes of wet chemical etching in diluted H_3PO_4 .

In Figure 5.13 (a) a pre-etched sample is shown, with the circular resist patterns of the first lithography already formed. During the growth of the multiple quantum wells, the bare ZnO substrates are clamped from their corners and therefore in that regions, indicated as the corner clip area, no growth occurs, and can be used as a ZnO reference. In Figure 5.13 (b) and (c) the effect the wet chemical etching has on the region where the multiple quantum wells are grown is shown, after 1 min and 6:20 min, respectively. The formation of grooves starts from the very first seconds of the etching process, and, as the etching time is increased, the grooves become deeper, making the sample useless to continue with the processing of QWIPs. Conversely, the corner clip area does not feature such grooves.

To have an idea of the roughness of the growth after the wet chemical etching, two depth profiles transversal to the grooves are shown in Figure 5.14.

Figure 5.14. Depth profiles of the grown heterostructure between two resist patterns, at the beginning and at the end of the wet chemical etching with diluted H_3PO_4 . The blue shaded regions indicate the presence of the resist on top of the surface.

Considering the structure of samples in Figure 5.12 (a), in order to reach the bottom ZnO:Ga contact layer the overall etched depth must be around 570 nm. However, as indicated, after 6:20 minutes the etched depth is about 210 nm (if the reference is taken at the top of the grooves) and the depth of the grooves is in the order of microns, making

the surface useless to continue with the processing. Much longer etching times are required to reach the desired depth of 570 nm, and the grooves will then be amplified.

Many attempts were made in order to find out the origin of the grooves and to avoid them: samples with lower Mg contents, with undoped ZnO QWs, and with lower overall (Zn,Mg)O thicknesses were tested with similar results. Besides, different acidic solutions were used in addition to H_3PO_4 , as for example diluted HCl, and even with different concentrations in volume. Up to now, the conclusion is that the wet chemical etching may be selective to the ZnO and (Zn,Mg)O layers, and hence it may cause the formation of grooves. Fortunately, an alternative to the wet chemical etching was found out within the partners of the ZOTERAC project (described in the next section), and further investigations related to the grooves were not carried out. The focus was put on the development of operating QWIPs.

5.4.3. New processing approach: dry etching by means of inductively coupled plasma etching

One of the advantages of working in a European project is the close collaboration between partners from different research institutions and the accessibility to alternative characterization and processing techniques, making possible to share knowledge and circumvent the arising problems. In the ZOTERAC project, the processing of mid-IR ZnO-based QWIPs was also carried out in the *Institut für Festkörperelektronik* of the *Technische Universität Wien* (TUW), an institution with a very wide background on processing devices, and the dry etching was proved by means of the inductively coupled plasma (ICP) technique. This may allow reducing the chemical impact on the surface and stimulate the physical etching.

It is worth to note that before sending the samples to TUW some attempts were made at ISOM also with the ICP etching technique, with SiH_4 , Cl_2 and Ar gases, but the grooves still appeared. The recipe used at TUW was based on CH_4 , a gas not available at ISOM.

The CH_4 -based recipe had the mixture of gases $\text{H}_2/\text{CH}_4/\text{Ar}$,¹⁴⁵ in a proportion of 3/30/3, and the obtained etching rates were of around 45 – 50 nm / min, low enough to have an accurate control of the final mesa depth. A SiN hard-mask was used, and the mask-to-ZnO selectivity was 1 to 10. Further details on the processing of QWIPs at TUW are beyond the scope of this chapter and can be found elsewhere.¹⁴⁶ After the processing, the samples were received at ISOM where the final steps for preparing them to be characterized were

carried out: cutting in $3 \times 3 \text{ mm}^2$ pieces, beveling at 45° , wire bonding, and packaging on TO-8 holders. A Nomarsky microscope top view of the final processed devices is shown in Figure 5.15.

Figure 5.15. Nomarsky microscope top view of several QWIPs processed in sample Q1 at TUW and encapsulated at ISOM. The three wire-bonded devices in this picture are numbered.

The extended contact pads facilitate the wire bonding. The wire-bonded devices share the same ground, in order to maximize the number of accessible devices, and the square top-contacts are wire-bonded separately. There are different mesa sizes electrically analyzed, from 10 to $100 \mu\text{m}$.

5.4.4. Dark IV characteristics

The dark current has a detrimental impact on the performance of the devices, since the photocurrent has to be detected over this background. Therefore, before measuring the photo-response, IV curves at room temperature (RT) were measured in several devices to know the order of magnitude of the dark current and discard short-circuited and damaged devices. The IV curves in dark conditions of several not-damaged devices with different mesa sizes corresponding to samples Q1, Q2, and Q3 are shown in Figure 5.16.

As observed, the current density has a symmetric behavior for negative and positive voltages and its magnitude is similar in the devices of samples Q1 and Q2 and about two orders of magnitude lower in the devices of sample Q3. This is an unexpected result since the differences in the design of the samples are minimal. The higher Mg content in the barriers of sample Q3 may have formed Mg-related defects acting as electron traps, as

discussed in Chapter 4, however, the drop of two orders of magnitude for the current density is still very high. Note that samples Q1 and Q2 belong to the same growth series while sample Q3 belongs to a different one, and therefore the environment during the growth and the processing may have changed, affecting the performance of the devices.

The leakage through the heterostructure or through the side-walls of the mesa is responsible for the dark current. However, there is a clear tendency in all samples for the density current to increase as the mesa area of the device is decreased. Therefore, the dark current is ascribed to proceed mainly from the side-wall current.

Figure 5.16. Logarithm of the current density vs applied voltage of several QWIPs tested in samples Q1 (a), Q2 (b), and Q3 (c). Note the different scale in (c). The legend indicates the mesa area for each color. For simplicity, for negative voltages the absolute values of the current density have been considered.

5.4.5. Photocurrent

The devices in sample Q3 have a lower dark current and its photocurrent results are shown in this section. From the pre-tested devices, those with lower dark current are

selected for measuring photocurrent at low temperature (LT), and correspond to devices with the largest mesa area, of $100 \times 10^{-6} \text{ cm}^2$. The current densities at RT and at LT of the measured devices are shown in Figure 5.17. Note that although the mesa area of the devices is the same, the current density at RT shows a variability of about one order of magnitude. Also, it can be observed how lowering the temperature yields a very significant drop of the current density, between 1 and 2 orders of magnitude. This phenomenon is ascribed to the lowering of the kinetic energy of electrons.

Figure 5.17. Logarithm of the current density vs applied voltage of several QWIPs of sample Q3 with a mesa area of $100 \times 10^{-6} \text{ cm}^2$, at room temperature (red) and at low temperature (blue). For simplicity, for negative voltages the absolute values of the current density have been considered.

Concerning the photocurrent measurements, they are carried out in the FTIR spectrometer in the photocurrent configuration described in Section 3.2.3. The sample is cooled down to 10 K and illuminated with the IR light from the SiC lamp, and each device is biased individually with voltages from 0 to 5 V. The photocurrent is converted to voltage with the I-V converter with a preselected gain. In order to select the proper gain, the order of magnitude of the dark current is considered, to avoid final voltages higher than 12 V, which is the maximum voltage input that the FTIR connector supports.

Unfortunately, the many attempts done in all the devices of the different samples gave the same result: no photocurrent resulting from the ISBT was detected. As an example of the measured spectra, the signal from a device of sample Q3 is shown in Figure 5.18.

Figure 5.18. Photocurrent signal of a processed device of sample Q3 with a mesa area of $100 \times 10^{-6} \text{ cm}^2$ measured with the FTIR spectrometer.

As observed, the signal is very noisy since the detected photocurrent is zero. Different bias and devices were tested with similar results.

Alternatively to the photocurrent measurements performed with the FTIR spectrometer, IV curves were tested under illumination (also with the SiC lamp), and some photocurrent was detected.

In Figure 5.19 (a), the current density flowing between the two contact layers of a QWIP of sample Q3 under different light conditions is shown. There is a small but detectable effect on the observed current density caused by the IR radiation, which can be better observed in Figure 5.19 (b). This effect is more pronounced for higher applied voltages and it is insensitive to light polarization: when the light is *s*-polarized the increase of the detected current density with respect to the dark conditions is similar to when the light is *p*-polarized. Thus, the photocurrent cannot be attributed to the ISBT and likely comes from free carrier absorption.

Figure 5.19. (a) Logarithm of the current density at 10 K in a device of sample Q3 with a mesa area of $100 \times 10^{-6} \text{ cm}^2$, under different light conditions: dark, illuminated, s- and p-polarized light. The inset shows a zoom at $\sim 1 \text{ V}$. (b) Difference between the current densities derived from (a).

Although in this section only the analysis performed in the processed devices of sample Q3 is shown, similarly, the two other designed and grown structures were analyzed with similar results. In addition, some attempts were made in samples belonging to series A and B of the previous section, and again no photocurrent coming from the ISBT was observed. From these results, the conclusion is that the high dark current observed in all the analyzed samples ($\sim 1 - 0.1 \text{ A cm}^{-2}$ at 1 V) may prevent the observation of photocurrent in QWIPs, which is expected to be orders of magnitude lower ($\sim 10^{-6} \text{ A cm}^{-2}$).

It must be noted that in the ZOTERAC project a quantum cascade detector (QCD) was finally demonstrated in the IR in collaboration with the *Université Paris Sud*, and the *Technische Universität Wien*.¹⁴⁶ Contrary to the QWIP, the QCD works under photovoltaic mode, and the dark current becomes extremely low, thus allowing the detection of the ISBT photocurrent.

Part III

Results: (Cd,Zn)O ternary

Chapter 6. Alloying CdO with ZnO in rock-salt phase

The results in this chapter are reproduced, with the permission of AIP Publishing, from the article “Rock-salt CdZnO as a transparent conductive oxide” published in the Applied Physics Letters journal, 113, 222101 (2018), by **J. Tamayo-Arriola**, A. Huerta-Barberà, M. Montes Bajo, E. Muñoz, V. Muñoz-Sanjosé, and A. Hierro.¹⁴⁷

The results were also presented by the author at the 10th International Workshop on Zinc Oxide and Other Oxide Semiconductors, celebrated in Warsaw, Poland, in September 2018.

6.1. Introduction

During the growth of CdO donor levels are formed, giving not only the n-type character to the material but also making it a degenerate semiconductor. Unexpectedly, the high electron concentration present in as-grown material does not reduce the electron mobility, yielding high conductivities. Thus, the intrinsic properties of CdO make it an excellent TCO, which can be employed in electronic applications where a high conductivity and transparency are required. Besides, in the field of plasmonics, materials with a high and tunable plasma frequency as well as a high optical electron mobility are required, and CdO fulfills these characteristics very well.

During the last years, many efforts have been done to improve the conductivity of CdO by doping it with other materials, such as In,³⁶ Dy,³⁸ or Sn.¹⁴⁸ An alternative may be to alloy it, for instance with ZnO, as some studies have tried.^{77,78,80,81} However, in polycrystalline materials, grain boundary scattering limits the enhancement of electron mobility, a key parameter for reducing the optical losses in a plasmonic material.

The aim of this chapter is to study the optical and electrical properties of the (Cd,Zn)O alloy in rock-salt phase, determining the optimum Zn content that maximizes the electrical conductivity whilst widening the transmission window of the material. To do so, Hall effect measurements, and IR reflectance and UV-VIS transmission spectroscopies are employed.

6.1.1. Sample description

The (Cd,Zn)O thin films were grown by MOCVD on *r*-plane sapphire substrates. Tertiary butanol, dimethylcadmium, and diethylzinc were used as O, Cd and Zn precursors, respectively, and the VI-II precursor ratio was kept at 5 in all the growths. This growth

technique can allow to achieve high crystal quality in the films for a substrate temperature as low as 330 °C. Nominal Zn contents range from 0 to 25 %, in steps of 5 %, and the Zn content was previously confirmed by energy-dispersive X-ray spectroscopy.¹⁴⁹ The thicknesses of the films are in the range between 120 and 200 nm.

6.2. Infrared reflectance spectroscopy

Due to the high free electron concentration in the (Cd,Zn)O films, the dielectric function of the material (and therefore the reflectance spectra) is mainly governed by the Drude term. As a result, the IR active phonon modes of the cubic structure of CdO, expected to be at 262 cm⁻¹ (TO) and 523 cm⁻¹ (LO), are not visible in the reflectance spectra and their contribution to the dielectric function can be neglected. Thus, the (Cd,Zn)O dielectric function is reduced to

$$\varepsilon^{(Cd,Zn)O}(\omega) = \varepsilon_{\infty}^{(Cd,Zn)O} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma_p}. \quad (6.1)$$

The only unknown parameters for each film are the plasma frequency, its damping factor, the high-frequency dielectric constant and the film thickness.

Regarding the sapphire dielectric function, the phonon modes utilized for modelling the reflectance spectra are the same as those deduced in Chapter 4, which reproduce well the features close to the reststrahlen band.

The reflectance spectra were measured at 45° angle of incidence in *p*-polarization and are shown in Figure 6.1, together with the curves obtained from the modelled dielectric function. The values of the fitted parameters are summarized in Table 6.1.

As the Zn content is increased, a shift in the reflectance minimum to higher frequencies is clearly observed, because of the increment of the plasma frequency (as defined in Eq. 2.17, $\omega_p = \sqrt{n e^2 / m_e^* \varepsilon_0}$), which reaches a value of 10125 cm⁻¹ for 25 % Zn. On the other hand, the broadening is reduced from 577 cm⁻¹ to 420 cm⁻¹ as 5 % Zn is added to CdO, whereas for larger Zn contents it increases monotonically, although is maintained below 600 cm⁻¹ for Zn contents up to 15 %. The degradation observed in samples with 20 and 25 % Zn is clearly seen in the reflectance spectra of Figure 6.1: the larger γ_p , i.e. the more damped the oscillating electrons, the slower they react to the incoming light, and therefore, the smaller the slope in the frequency region below the reflectance minimum.

Since the optical mobility is inversely proportional to γ_p , as $\mu_{opt} = e/m_e^* c \gamma_p$, its trend is the opposite and decreases monotonically for Zn contents above 5 %. However, optical mobilities for Zn contents up to 15 % are higher than previously reported values in CdO.³⁰

The high-frequency dielectric constant deduced from the fits starts at 5.3 for CdO,³⁰ decreasing as the Zn content increases. Indeed, $\epsilon_{\infty}^{ZnO} = 3.69$ ¹² and the fitted values match well an interpolation between the ϵ_{∞}^{CdO} and ϵ_{∞}^{ZnO} values.

Figure 6.1. Reflectance spectra (continuous lines) and fits (dotted lines) in *p*-polarization at 45° angle of incidence of the (Cd,Zn)O alloys.

Sample	Fitted parameters			Derived parameter
Zn content (%)	ω_p (cm ⁻¹)	γ_p (cm ⁻¹)	ϵ_{∞}	μ_{opt} (cm ² V ⁻¹ s ⁻¹)
0	6851	577	5.30	519
5	8704	420	5.22	695
10	9319	466	5.10	633
15	9705	547	5.06	536
20	10125	875	4.96	334
25	10125	934	4.74	316

Table 6.1. For each Zn content (left column), values of the fitted parameters from reflectance spectroscopy (center column) and calculated optical mobility (right column).

6.3. Transport characteristics

Hall effect measurements at room temperature were carried out in the (Cd,Zn)O thin films, in order to derive n_{Hall} , μ_{Hall} , and ρ . The results are shown in Figure 6.2.

Figure 6.2. Dependence of the Hall electron concentration, Hall mobility, and resistivity on the Zn content.

The Hall mobility values are approximately six times smaller than those of the optical mobility (see Table 6.1), a phenomenon observed previously in CdO.³⁰ As discussed in Chapter 4 for the (Zn,Mg)O alloy, in Hall effect measurements the electrons travel microscopically and are affected by extended defects to a greater extent than with reflectance measurements. Nevertheless, the overall evolution of μ_{Hall} with the Zn content is similar than that obtained for μ_{opt} : first an enhancement from CdO to the alloy with 5 % Zn, followed by a gradual decrease for larger Zn concentrations. The increase of μ_{Hall} for low contents with respect to that of CdO, achieving values around $110 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, contrasts the sudden decrease in μ_{Hall} found elsewhere for polycrystalline (Cd,Zn)O films,^{79,80} yielding very low resistivities. As happens with the optical mobility, it is only for Zn contents larger than 15 % that μ_{Hall} drops drastically.

The mobility results obtained here correlate with the results from high-resolution x-ray diffraction (HRXRD) measurements performed on the same samples by Huerta-Barberà *et al.*¹⁴⁹ From HRXRD, a single-oriented cubic crystalline orientation (002) was detected for Zn contents up to 10 %. This peak shifts with increasing Zn content up to 15 %, indicating

the incorporation of Zn in the ternary alloy. From 15 to 25 % Zn, peaks corresponding to different cubic orientations ((111) and (220)) arise, as well as an additional peak (0002) coming from the wurtzite phase for $\text{Zn} \geq 20\%$. Hence, the (Cd,Zn)O ternary shows a cubic phase with a single crystal orientation up to 10 % Zn, whereas at 15 %, the cubic crystals start to be orientated in different directions. Only for high Zn contents, above 20 %, peaks corresponding to both rock-salt and wurtzite crystalline structures were observed. Thus, the high crystal quality achieved in samples up to 10 % Zn explain well the low resistivity here reported, whereas the degradation of the electron transport and optical mobilities for $\text{Zn} \geq 15\%$ likely results from grain boundary scattering and eventually from the coexistence of rock-salt and wurtzite phases. Details of the structural characterization of these samples can be found elsewhere.¹⁴⁹

As shown in Figure 6.2, the values for n_{Hall} are always above $1 \times 10^{20} \text{ cm}^{-3}$ with an upward trend with the Zn content, reaching a maximum of $3.9 \times 10^{20} \text{ cm}^{-3}$ for 20 % Zn. This trend has already been observed before in (Cd,Zn)O polycrystalline films but with lower absolute values.^{79,80} The increment in n_{Hall} with Zn may respond to the formation of intrinsic defects. In CdO, two main sources of electrons are commonly accepted: oxygen vacancies (V_o), introducing shallow levels and acting as doubly-ionized donors, and hydrogen impurities, in the form of interstitials (H_i) and behaving as single-ionized donors.^{66,68} As calculated by Burbano *et al.* for pure CdO and Cd-poor/O-rich conditions, as it is the case in this study, H_i are the defects with the lower formation energy for the Fermi level energies obtained in the analyzed samples, whereas V_o have positive formation energies. Following the same argument as in ZnO when Mg is incorporated in the structure,¹⁵⁰ as Zn is added to the cubic CdO structure, the unit cell becomes smaller, and the electrostatic repulsion resulting from the creation of V_o increases, causing a further increase in its formation energy. Thus, the incorporation of Zn into CdO is expected to further increase the formation energy of V_o , pointing at H_i as the main donor. This H atoms may originate from the precursors used during the growth, $(\text{CH}_3)_2\text{Cd}$ and $(\text{C}_2\text{H}_5)_2\text{Zn}$ for Cd and Zn, respectively. Hence, the growth of the (Cd,Zn)O ternary is carried out under an environment richer in H compared to CdO, which may enhance the formation of H_i .

Regarding the resistivity, the achieved values for the ternary (Cd,Zn)O are comparable to those from state-of-the-art highly developed TCOs, including $\text{In}_2\text{O}_3:\text{Sn}$, $\text{ZnO}:\text{Ga}$, $\text{ZnO}:\text{Al}$, or $\text{ZnO}:\text{In}$,²⁸ but those, in general, require much higher growth temperatures than (Cd,Zn)O, which is a barrier for their integration on foreign devices. Indeed, as the Zn

content is increased in the ternary alloy, the resistivity decreases from $5 \times 10^{-4} \Omega \text{ cm}$ in CdO to as low as $1.95 \times 10^{-4} \Omega \text{ cm}$ in the alloy with 10 % Zn. These resistivities are found to be the lowest reported values for the (Cd,Zn)O alloy^{77–81} and comparable to those obtained in CdO doped with different donors such as F,³⁴ Al,³⁵ Sn,³⁷ or Dy,³⁸ whose results are summarized in Table 6.2.

Material	Growth method	$\mu \text{ (cm}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}$	$n \text{ (} \times 10^{20} \text{ cm}^{-3}\text{)}$
CdO:F, ³⁴ polycrystalline	Sol-gel (350 °C)	~ 60	~ 11
CdO:Al, ³⁵ s polycrystalline	Sol-gel (350 °C)	~ 54	~ 3.2
CdO:Sn, ³⁷ single-oriented	PLD (750 °C)	~ 300	~ 10
CdO:Dy, ³⁸ single-oriented	MBE (350 °C)	~ 350	~ 2
(Cd,Zn)O, this work	MOCVD (330 °C)	~ 110	~ 3

Table 6.2. Summary of the growth and electrical properties of reported CdO-based materials for their integration as TCOs.

It is worth to note that, the CdO:F and CdO:Al films are polycrystalline and therefore their mobilities were found to be low. On the other hand, very high mobilities were achieved in CdO:Sn and CdO:Dy films with a single cubic orientation detected by x-ray measurements, but the former material requires a very high growth temperature, which could be a problem in case the TCO has to be integrated in a potential device.

6.4. Optical bandgap

In a TCO, the optical bandgap determines the range of wavelengths on which the material is transparent in the visible, and here is determined by means of UV-VIS transmission spectroscopy.

In Figure 6.3 the transmittance spectra of the thin films are shown. It can be observed how the transmission edge shifts to higher energies when the Zn content is increased, and below it, the transmittance rises to values between 70 – 80 %, as in typical TCOs. From the transmittance spectra and using the Beer-Lambert law (Eq. 3.1) the absorption spectra is deduced and shown in Figure 6.4 (a), from where the optical bandgap is obtained taking the maximum of its derivative (Figure 6.4 (b)).

Figure 6.3. Transmittance spectra of the (Cd,Zn)O alloys. The inset shows the region of interest where the transmittance starts rising.

Figure 6.4. (a) Absorption coefficient vs energy, and (b) its normalized derivative, for all Zn contents.

The optical bandgap shifts to larger energies when adding Zn, reaching 2.89 eV for 15 % Zn, around 0.3 eV larger than that of CdO. Thus, the transparency in the visible of the ternary alloy increases with respect to that of CdO. As occurs with the electron mobility, the films with the highest Zn contents, 20 and 25 %, do not follow the trend and also the

peak of the absorption derivative is wider, which correlates with the degradation of the crystal quality of the alloy observed in the x-ray measurements.

6.4.1. Derivation of the bandgap at Γ point

The large blue-shift of the optical bandgap with Zn results from both the modification of the band structure and the rise in the free electron concentration, which shifts the Fermi level energy well above the CB minimum. Regarding the latter, also known as the Burstein-Moss shift and described in Section 3.3.2, the contribution can be computed with

$$E_{BM} = \left(\frac{\hbar^2}{2m_e^*} \right) (3\pi^2 n)^{\frac{2}{3}}. \quad (6.2)$$

At this point it is necessary to have an accurate value of the electron effective mass at the E vs k point where the Fermi level is placed, accounting for the CB non-parabolicity. Thus, m_e^* is calculated from the plasma frequency, assuming $n_{opt} = n_{Hall}$, which, as shown in Chapter 4 for the (Zn,Mg)O alloy, is typically valid when the free electron concentration is very large compared to the concentration of defects acting as acceptor traps. The resulting effective masses are shown in Figure 6.5.

Figure 6.5. Dependence on the Zn content of the measured optical bandgap, the calculated bandgap energy at the Γ point considering the Burstein-Moss shift from Eq. 6.2, and computed electron effective mass using from the plasma frequency. The shaded area indicates the Zn contents at which phase segregation starts.

The value of $\sim 0.27m_0$ extracted for the CdO reference film is in excellent agreement with that reported by Jefferson *et al.*²⁹ for CdO with $n \sim 1.5 \times 10^{20} \text{ cm}^{-3}$ where the CB non-parabolicity was also accounted for.

The bandgap energy at the Γ point after the subtraction of E_{BM} to the optical bandgap is also presented in Figure 6.5. The bandgap of the reference CdO film matches quite well the value of $\sim 2.17 \text{ eV}$ given by Jefferson *et al.* for CdO films grown by MOCVD.²⁹ Then, it increases with the Zn content but at a much lower rate than the optical bandgap, as would be expected from a linear interpolation from the CdO to the ZnO bandgaps. However, a proper calculation of this interpolation requires to know the bandgap of rock-salt ZnO at the Γ point, but since ZnO is not stable in this crystal structure, its value is not well known. The calculation by Schleife *et al.*¹⁵¹ yields a corrected indirect bandgap of 2.6 eV for rock-salt ZnO, close to the value determined experimentally by Segura *et al.*,⁶⁹ and a direct bandgap at the Γ point of around 4 eV , also not too far from the measured absorption at $\geq 4.5 \text{ eV}$ by Segura *et al.*, which they ascribed to the same origin. With these values, the linear interpolation yields an incorporation of Zn of 9 – 10 % in the rock-salt (Cd,Zn)O film where the energy-dispersive X-ray technique yields a 15 %.

6.5. Conclusion

In this study, the electrical and optical properties of the (Cd,Zn)O ternary have been evaluated as a function of the Zn content. The (Cd,Zn)O alloy shows improved characteristics as compared to pure CdO and other common TCOs, being an excellent candidate for becoming a TCO and an IR plasmonic material.

The growth of this ternary by MOCVD allows to obtain high crystal quality thin films with large mobility and free electron concentration and therefore low resistivity, as low as $1.95 \times 10^{-4} \Omega \text{ cm}$ for the film with 10 % Zn. In Figure 6.6 a comparison of the resistivities obtained by doping or alloying CdO with other materials is shown.

As observed, in the (111)-oriented CdO:Sn films grown by pulsed laser deposition the electrical resistivity is reduced down to $2 \times 10^{-5} \Omega \text{ cm}$. However, the required growth temperature is 750°C , making the integration of this TCO in a real device really challenging. On the other hand, the result in this work is an order of magnitude lower than the best result for the (Cd,Zn)O alloy, and even with a lower growth temperature, and comparable with resistivities and growth temperatures of single-phase CdO:Dy films.

Figure 6.6. Comparative of the resistivities obtained by doping of alloying CdO with other materials, vs their growth temperature.

Moreover, the optical bandgap shifts to much larger energies with Zn as a result of the Burstein-Moss shift, spreading out from 2.58 eV for CdO to 2.89 eV for the film with 15 % Zn, and thus increasing the transparency of the TCO in the visible.

Chapter 7. Surface polaritons in the (Cd,Zn)O alloy

The results in this chapter have been accepted for their publication in the ACS Photonics scientific journal (September 2019), with title "A controllable and highly propagative hybrid surface plasmon-phonon polariton in a CdZnO-based two-interface system", by **J. Tamayo-Arriola**, E. Martínez Castellano, M. Montes Bajo, A. Huerta-Barberà, E. Muñoz, V. Muñoz-Sanjosé, and A. Hierro. The results were also presented by Julen Tamayo Arriola and Eduardo Martínez Castellano at the META 2019 International Conference, in Lisbon, Portugal, in July 2019.

7.1. Introduction

7.1.1. Motivation

The outstanding properties of electromagnetic surface waves and the recent progress in the synthesis of semiconductors with optimized properties has renewed the interest in the field of plasmonics and its application to new photonic devices.^{152–154} As a result, there is a growing demand for functional photonic devices based on light-matter interaction at interfaces that can overcome the limitations of the current technology of semiconductor integrated circuits,¹⁵⁵ exploring the light confinement phenomenon beyond the diffraction limit.¹⁵⁶

Light interaction with doped semiconductors and polar dielectrics leads to the formation of surface plasmon polaritons (SPPs) and surface phonon polaritons (SPhPs), respectively. In such media, when the thickness is comparable to the optical skin depth (δ) (the distance at which the field is attenuated by a factor of $1/e$), epsilon-near-zero (ENZ) modes arise at the frequency where the dielectric function vanishes.¹⁵⁷ While ENZ modes have the extraordinary ability to confine light within sub-wavelength thin films,¹⁵⁸ and therefore are suitable for photovoltaics and bolometer devices¹⁵³ and for nonlinear optics,¹⁵⁴ they lack the property of being dispersive, and thus show very low group velocities and propagation lengths. Conversely, SPPs and SPhPs have lower light confinements, but much larger group velocities, a key point when signal transport along an interface is required, as in plasmonic waveguides.¹⁵⁵ Thus, surface polaritons suffer from the trade-off between confinement and propagation, and, in the attempt to overcome it, in this chapter the hybridization of SPPs with SPhPs in the air-(Cd,Zn)O-sapphire three-layer system with very low optical losses has been

experimentally and theoretically explored, looking for the enhancement of the propagation length of the hybrid mode as compared to the bare SPP and without loss of confinement.

The frequencies of the surface modes studied in this chapter fall in the mid-IR range of the electromagnetic spectrum, which, as mentioned in Chapter 1, is widely used in spectroscopy and molecular sensing, since the rotational and vibrational frequencies of many molecules and crystalline structures fall in that range.¹⁵⁹ While plasmonics in the visible and near-IR ranges has been extensively studied,¹⁵⁵ in the mid-IR range few plasmonic devices have been experimentally demonstrated.^{160,161} Hence the importance of developing new compact and efficient lab-on-chip photonic devices for molecular sensing, where electromagnetic surface modes can be used to build plasmonic waveguides transporting signal from the light source to the detector while sensing the adjacent medium.^{161,162}

Ideal plasmonic materials for mid-IR applications should have a tunable electron concentration between 10^{19} and 10^{21} cm^{-3} and a high electron optical mobility, which yields a tunable and narrow plasma resonance. Noble metals such as Ag and Au have been widely studied in the field of plasmonics, however, their high plasma frequencies falling in the ultraviolet makes them behave as perfect conductors in the mid-IR, preventing the subwavelength confinement of the surface modes.^{159,163,164} In addition, the electron concentration of noble metals cannot be tuned, and the only way of shifting their plasma resonance to the mid-IR is developing complex-shaped metallic nanostructures. The best alternative materials for mid-IR plasmonics are TCOs, with a tunable plasma resonance in the mid-IR and a high electron mobility.¹⁶⁵

However, typical TCOs such as ITO and ZnO are far from being ideal for mid-IR plasmonics due to their high plasma dampings ($\sim 800 - 900$ cm^{-1}),^{115,166} which result in low optical mobilities. In this sense, CdO fulfills the requirements and is postulated to be the best candidate among all TCOs, taking advantage of its high electron concentrations and high optical mobilities in as-grown material.^{29,30} Therefore, this chapter aims to be the continuation of Chapter 6, where the evolution of the transport and optical properties of the (Cd,Zn)O alloy as a function of the Zn content were studied, and the optimum Zn content for mid-IR plasmonics was determined.

7.1.2. A controllable hybrid mode

In this chapter, a detailed analysis of the hybridization of two distinct-in-nature surface modes is presented: the SPP, produced by (Cd,Zn)O, a plasmonic oxide, and the SPhP, produced by sapphire, a polar dielectric crystal, which also serves as the substrate where the (Cd,Zn)O film is epitaxially grown. The resulting hybrid mode, the surface plasmon-phonon polariton (SPPP), first proposed by M. Nakayama,¹⁶⁷ takes advantage of both the bare phonon and plasmon surface modes, being a confined and highly propagative surface mode excitable in a wide range of attainable frequencies. The SPPP hybrid mode has been experimentally observed, among other 2D systems, at the graphene-boron nitride interface, confined in extremely small volumes.¹⁶⁸ Here the first experimental observation of SPPPs in oxides is presented, much easier to synthesize than graphene and with extraordinary electrical properties for their implementation in the aforementioned plasmonic devices. Moreover, as compared to a graphene plasmonic monolayer, the thickness and plasma frequency of thin film oxides can be easily controlled, which allows modulating the optical response of the SPPP modes over a wide range of frequencies in the mid-IR.

In the air-(Cd,Zn)O-sapphire three-layer system here explored, the coupling strength of the fields at the air-(Cd,Zn)O and (Cd,Zn)O-sapphire interfaces is easily controlled by the (Cd,Zn)O thickness. This coupling leads to the well-known symmetric and antisymmetric field distributions, as schematized in Figure 7.1, which appear at different energies.^{158,169,170}

Figure 7.1. Instantaneous distribution of the z-component of the electric field of the surface modes in the air-(Cd,Zn)O-sapphire system. (a) Decoupled interface modes for (Cd,Zn)O thicknesses much higher than the (Cd,Zn)O skin depth, (b) symmetric mode and (c) antisymmetric mode formed for (Cd,Zn)O thicknesses comparable to the (Cd,Zn)O skin depth.

Note that the studied system is not perfectly symmetric, since the dielectric functions of air and sapphire are different, but here it refers to the symmetry of the sign of the field distributions, for simplicity. The most energetic mode, i.e. the symmetric mode, shifts to higher energies when the (Cd,Zn)O thickness is reduced, and it is pinned at the (Cd,Zn)O plasma frequency in the extremely thin case. It corresponds to the ENZ mode, where the dielectric function of (Cd,Zn)O vanishes. The less energetic mode, i.e. the antisymmetric mode, which in fact is the SPPP, turns from a plasmon-like behavior for frequencies far from the sapphire phonons in the thickest (Cd,Zn)O film to a phonon-like behavior as the thickness of the film is reduced and the coupling of the fields at both interfaces becomes stronger. Precisely, in the thinner (Cd,Zn)O films the effect of the sapphire phonons is more evident, with a direct effect on the enhancement of the propagation length of the SPPP mode. In the ultrathin limit case, the surface mode is dominated by the sapphire SPhP. As shown in Section 4.2 sapphire has several phonon modes, but the one hybridized with the surface plasmon polariton is the most energetic one, with its TO mode at 633 cm^{-1} and its longitudinal optical LO mode at 905 cm^{-1} .

7.1.3. Sample design

The (Cd,Zn)O alloys, which act as the plasmonic materials, were grown on *r*-plane sapphire substrates by MOCVD. The samples were grown at *Universitat de València*.

The Zn content was set to 10 %, which ensures a high plasma frequency falling in the mid-IR ($\sim 4000\text{ cm}^{-1}$), as well as a low plasma damping, of about $\sim 500\text{ cm}^{-1}$, resulting in an optical mobility of about $\sim 600\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, as revealed in the previous chapter. To study the coupling of the fields at the air-(Cd,Zn)O and (Cd,Zn)O-sapphire interfaces and analyze the formation of the surface modes, a total of five samples with different (Cd,Zn)O thicknesses were grown, experimentally determined to be 25, 65, 150, 250 and 460 nm-thick.

7.2. Results and discussion

7.2.1. Reflectance measurements and modelling

Following the same procedure as in Section 6.2, the IR reflectance spectra of the samples were measured and fitted in order to obtain the fundamental parameters of the (Cd,Zn)O films and the sapphire substrate: the (Cd,Zn)O plasma frequency and its damping, the (Cd,Zn)O film thickness (d) and the sapphire phonon modes. The dielectric function of each constituent layer was modelled and the TMM was applied.

First, the *r*-plane sapphire substrate was measured and fitted, and its phonon modes were derived. The model for the dielectric function of sapphire is similar to that described in Chapter 4 (Eq. 4.6), so it is not repeated here. Both in the reflectance and attenuated total reflectance (ATR) measurements, the sapphire substrate was oriented in the direction where the *A* phonons are minimized,¹²¹ and therefore to fit the reflectance and ATR spectra only its *E* phonons are required, whose values can be found in Table 4.1.

Concerning the Drude model used for fitting the reflectance and ATR curves of the (Cd,Zn)O alloys, in this chapter a subtle difference is implemented with respect to previous chapters. In the literature, the plasma frequency is found to be defined in two different ways, with and without considering the high-frequency dielectric constant, as

$$\omega_{p,1} = \left(\frac{ne^2}{m_e^* \epsilon_0} \right)^{1/2} \quad (7.1.a)$$

$$\omega_{p,2} = \left(\frac{ne^2}{m_e^* \epsilon_0 \epsilon_\infty} \right)^{1/2}. \quad (7.1.b)$$

Then, the dielectric function of the material would be expressed, respectively, as

$$\epsilon(\omega)_1 = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma_p \omega} \quad (7.2.a)$$

$$\epsilon(\omega)_2 = \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma_p \omega} \right). \quad (7.2.b)$$

Both expressions are valid, and, when the frequency at which the dielectric function vanishes in Eqs. 7.2.a and 7.2.b has to be derived, i.e. $\epsilon(\omega_{1,2})_{1,2} = 0$, the resulting frequency is the same in both cases, having the contribution of ϵ_∞ (note the damping of the plasma frequency was set to zero, for simplicity), as

$$\omega_1 = \left(\frac{\omega_{p,1}}{\epsilon_\infty} \right)^{1/2} = \left(\frac{ne^2}{m_e^* \epsilon_0 \epsilon_\infty} \right)^{1/2} \quad (7.3.a)$$

$$\omega_2 = (\omega_{p,2})^{1/2} = \left(\frac{ne^2}{m_e^* \epsilon_0 \epsilon_\infty} \right)^{1/2} \quad (7.3.b)$$

Thus, $\omega_1 = \omega_2$, frequency at which the reflectance minimum corresponding to the oscillating electrons is observed. Although in previous chapters the used definition of the plasma frequency was that in Eq. 7.1.a, with the dielectric function in Eq. 7.2.a, in this chapter the definition in Eq. 7.1.b is employed, with the dielectric function in Eq. 7.2.b, since it would be more intuitive in order to match the polariton resonances observed in the reflectance and ATR spectra with the frequencies predicted with the modelling.

The measured and modelled reflectance curves of all the samples are shown in Figure 7.2, and the extracted values from the fits are shown in Table 7.1.

Figure 7.2. Reflectance spectra (continuous lines) and fitted model (dotted lines) of all the samples at 45° in *p*-polarization, offset for clarity. The plasma frequency of the thickest (Cd,Zn)O film is indicated as an example, falling at the dip in the reflectance spectrum.

a (nm)	ω_p (cm ⁻¹)	γ_p (cm ⁻¹)
460	4082	525
250	4121	518
150	4043	518
65	4098	550
25	3980	503

Table 7.1. Values of the fitted parameters of the (Cd,Zn)O films from reflectance spectroscopy. A value of $\epsilon_{\infty}^{(\text{Cd,Zn})\text{O}} = 5.1$ was obtained for all films.

As can be observed in Table 7.1, except for the thickness, all the other fitted parameters are very similar in all the (Cd,Zn)O films. Therefore, essentially all the changes in the reflectance spectra arise from the variation of the (Cd,Zn)O thickness. Besides, it is worth to note the difference between the damping of the (Cd,Zn)O plasmons and that of sapphire phonons. While in (Cd,Zn)O the plasmons have dampings around 520 cm^{-1} , the E_4 phonon mode of sapphire has a damping of 6 cm^{-1} for the TO and 17 cm^{-1} for the LO (see Table 4.1). Thus, the damping of the SPPP hybrid mode must be between these two limits, depending on the proximity of the resonance to the sapphire phonons.

All the parameters derived from the reflectance fits were used as input parameters for the ATR simulations, in order to compare the modelled ATR curves with the experimental ones.

7.2.2. Attenuated total reflectance measurements and modelling

In order to excite the surface resonances, ATR measurements were carried out in the FTIR spectrometer. The incident light was p -polarized and its in-plane momentum was matched to that of the polariton, k_x , by using a ZnSe prism with an internal angle of 45° in the Otto configuration,¹⁷¹ as schematized in Figure 7.3.

Figure 7.3. Schematic of the ATR measurements carried out in the Otto configuration. The evanescent wave generated at the prism-air interface excites the surface modes of the air-(Cd,Zn)O-sapphire system. The z -component of the electric field of the symmetric mode is represented.

The angle of incidence at the prism-air interface, denoted in Figure 7.3 as θ , was controlled from 39° to 59° , allowing to scan the polariton dispersion curve through $k_x = k_0 n_p \sin \theta$, where $n_p = 2.37$ is the prism refractive index and k_0 the light momentum in air.

The measured ATR curves of all samples are shown in Figure 7.4, and, in order to compare them with those modelled with the TMM, the simulated ATR curves are shown in Figure 7.5. The parameters for modelling the ATR curves are taken from the reflectance measurements, and the only parameter to be fitted is the air gap, which results to be about 350 nm in all the experiments, small enough to excite the SPPP and large enough to nearly decouple the prism-air interface from the system. In each case, the upper branch (UB), corresponding to the symmetric mode, and the lower branch (LB) corresponding to the antisymmetric mode, the SPPP, are indicated.

Comparing Figure 7.4 with Figure 7.5, the shape of the measured and modelled ATR curves is very similar in both cases, and the frequencies of the LB and the UP are in excellent agreement.

Figure 7.4. From (a) to (e), ATR measured curves for decreasing (Cd,Zn)O thickness. The angle of incidence was varied in the range from 39° (dark color) to 59° (light color). (f) ATR measured curve of the *r*-plane sapphire substrate. The inset shows in more detail the sapphire SPhP.

Figure 7.5. From (a) to (e), ATR simulated curves with the TMM for decreasing (Cd,Zn)O thickness. The angle of incidence was varied in the range from 39° (dark color) to 59° (light color). (f) ATR simulated curve of the *r*-plane sapphire substrate. The inset shows in more detail the sapphire SPhP.

First, the two (Cd,Zn)O extreme thicknesses are considered, i.e. 460 and 25 nm. In the thickest (Cd,Zn)O film (Figure 7.4 (a)), the air-(Cd,Zn)O and the (Cd,Zn)O-sapphire interfaces are almost fully decoupled, and the system behaves as having two independent interface layers, each with its surface mode: the SPP formed at the air-(Cd,Zn)O interface corresponding to the UB, and the SPPP formed at the (Cd,Zn)O-sapphire interface corresponding to the LB. Also, it can be seen how the LB is almost negligible, owing to the exponential decay of the evanescent wave within the (Cd,Zn)O, which hardly reaches the (Cd,Zn)O-sapphire interface.

On the other hand, in the 25 nm-thick (Cd,Zn)O film (Figure 7.4 (e)) the fields at both interfaces are coupled and arrange in a symmetric distribution for the SPP (UB), and in an antisymmetric distribution for the hybrid SPPP (LB). As a result, compared to the modes formed in thicker (Cd,Zn)O films, the difference in energy of the two branches increases, and the reflectance drop in the antisymmetric branch becomes narrower and more pronounced, while the symmetric branch losses prominence. This is a consequence of two facts: first, the thickness of the plasmonic material is reduced and so does the strength of its associated SPP; second, the SPPP hybrid mode acquires a phonon-like character with a

lower plasmon-phonon damping. Indeed, from the reflectance measurements the damping of the plasma frequency was deduced to be $\sim 525 \text{ cm}^{-1}$ and the dampings of the TO and LO phonons 6 and 17 cm^{-1} , respectively. Therefore, the damping of the hybrid mode is expected to vary between these two limits, depending on the proximity of the resonance to the sapphire phonons.

The overall evolution of the two branches with the thickness of the (Cd,Zn)O film can be better observed in Figure 7.6, where the ATR contour plots of all the samples are shown.

Figure 7.6. From (a) to (f), simulated ATR contour plots and experimentally determined resonance frequencies (circular dots) in *p*-polarization for the air-(Cd,Zn)O-sapphire three-layer system, for each (Cd,Zn)O thickness. The horizontally dotted lines indicate for each sample, from the highest to the lowest frequency: the plasma frequency (ω_p), the asymptote of the bare surface plasmon polariton formed at the (Cd,Zn)O-air interface ($\omega_{\text{SPP, (Cd,Zn)O-air}}$), the asymptote of the bare surface plasmon polariton formed at the (Cd,Zn)O-sapphire interface ($\omega_{\text{SPP, (Cd,Zn)O-sapphire}}$), and the asymptote of the bare surface phonon polariton formed at the sapphire-air interface ($\omega_{\text{SPhP, sapphire-air}}$). The inset in (f) shows in more detail the reststrahlen band of the most energetic sapphire phonon, where the SPhP is found.

The plots in Figure 7.6 were modelled by applying the TMM to the air-(Cd,Zn)O-sapphire system with a ZnSe prism on top, and the symbols indicate the resonances experimentally obtained.

Starting with the thickest (Cd,Zn)O film (Figure 7.6 (a)), the UB is a pure plasmonic mode, and has an asymptote at $\omega_{SPP, (Cd,Zn)O-air} = \omega_p \cdot (1 + \epsilon_{\infty}^{(Cd,Zn)O})^{-1/2}$ when the in-plane momentum goes to infinity. On the other hand, although the LB is almost negligible, it corresponds to the hybrid SPPP mode, with a phonon-like behavior for lower in-plane momentum and a plasmon-like behavior with an asymptote at $\omega_{SPP, (Cd,Zn)O-sapphire} = \omega_p \cdot (\epsilon_{\infty}^{Sapphire} + \epsilon_{\infty}^{(Cd,Zn)O})^{-1/2}$ for higher in-plane momentum.

As can be observed in Figure 7.6 from (b) to (e), as the thickness decreases the fields at both interfaces start to interact, resulting in the separation of the symmetric and antisymmetric branches. The symmetric one (UB) approaches the ENZ mode, where the dielectric function of the material vanishes at the plasma frequency, appearing only for thicknesses below the skin depth of the material. In fact, it can be seen how in the 25 nm-thick (Cd,Zn)O layer, the resonances of the UB appear at 3850 cm^{-1} , very close to the plasma frequency ($\sim 3970 \text{ cm}^{-1}$). If the thickness were further reduced, the resonances would be pinned at the plasma frequency. In contrast, the antisymmetric branch (LB) approaches the reststrahlen band formed within the sapphire TO and LO phonons for reduced thicknesses. Indeed, for the thinnest (Cd,Zn)O film the behavior of the LB approaches that of the pure sapphire surface phonon polariton shown in Figure 7.6 (f), confined within the reststrahlen band, from the TO phonon for low in-plane momentum to the asymptote at $\omega_{SPP} = 845 \text{ cm}^{-1}$ when the in-plane momentum tends to infinity. At the resonance, the fraction of the reflected light is close to zero, acting as a nearly-perfect absorber.

7.2.3. Dispersion curves

In order to properly evaluate the effect of sapphire phonons on the hybrid mode, the dispersion curves of the modes have been derived. To do so, the real part of the in-plane momenta of the surface modes are calculated. While the air-(Cd,Zn)O-sapphire system is enough to qualitatively describe the nature of the surface polaritons, in order to accurately derive the dispersion curves of the SPPP the prism has also to be considered, i.e. air is considered with a finite thickness, and the ZnSe prism is treated as a semi-infinite medium.

Following the derivation deduced by Baltar *et al.*,¹⁷² $Re\{k_x, k_z\}$ and $Im\{k_x, k_z\}$ in a three-interface system can be obtained from

$$\det \begin{vmatrix} R_1 e^{-\kappa_2(a+b)} - R_2 e^{-\kappa_2(a+b)} & R_1 e^{\kappa_2(a+b)} + R_2 e^{\kappa_2(a+b)} & 0 & 0 \\ 0 & 0 & R_4 + R_3 & R_4 - R_3 \\ e^{-\kappa_2 a} & e^{\kappa_2 a} & -e^{-\kappa_3 a} & -e^{\kappa_3 a} \\ R_2 e^{-\kappa_2 a} & -R_2 e^{\kappa_2 a} & -R_3 e^{-\kappa_3 a} & R_3 e^{\kappa_3 a} \end{vmatrix} = 0. \quad (7.4)$$

The zeros of the determinant define the implicit relation between $Re\{k_x, k_z\}$ and $Im\{k_x, k_z\}$ with the frequency of the incident light. Letters a and b indicate the thickness of the (Cd,Zn)O film and the air gap, respectively, and the subscript numbers are related to the involved materials: 1 for the ZnSe prism, 2 for air, 3 for (Cd,Zn)O and 4 for sapphire. The different parameters are defined as:¹⁷²

$$\kappa = ik_z = \sqrt{k_x^2 - \epsilon k_0^2} \quad \text{with} \quad k_0 = \omega/c, \quad (7.5)$$

where c is the speed of light, and

$$R_i = \kappa_i / \epsilon_i, \quad (7.6)$$

where the subscript i takes the number of the corresponding layer and ϵ_i is its associated dielectric function.

In Figure 7.7, the dispersion curves of the air-(Cd,Zn)O-sapphire system with variable (Cd,Zn)O thicknesses are compared to that of an idealized system on which phonons have been removed from the sapphire dielectric function, i.e. the sapphire substrate is substituted by a dielectric with a constant dielectric function equal to 3, which indeed is the high-frequency dielectric constant of sapphire, $\epsilon_\infty^{\text{sapphire}}$.

The range of frequencies where the LB is visible is clearly modified by the effect of sapphire phonons, as observed when comparing Figure 7.7 (a) and (b). Moreover, the LB is much more dispersive with a phonon-free dielectric substrate, yielding a pure SPP, and for small variations of the angle of incidence, the shift of the resonance is considerable. This could indicate a higher propagation length (L_p) of the pure SPP mode along the x -axis compared to the hybrid SPPP, since the group velocity, defined as $v_g = \partial\omega / \partial Re[k_x]$, is higher. However, as discussed below, thanks to the reduced damping of the hybrid SPPP mode compared to the SPP, its losses are reduced and therefore its L_p is largely enhanced.

Figure 7.7. Lower branch dispersion curves computed with the TMM for all (Cd,Zn)O thicknesses for (a) the air-(Cd,Zn)O-sapphire system, where the circular symbols indicate the measured frequencies, and (b) the idealized air-(Cd,Zn)O-dielectric system, where the dielectric function of sapphire is free of phonon resonances. The shaded blue regions indicate the measurable range with the ZnSe prism, at an angle of incidence from 39° to 59°. The dashed line represents the light line at 45° angle of incidence with the ZnSe prism. (c) ATR measurements and simulations of the air-(Cd,Zn)O-sapphire and idealized air-(Cd,Zn)O-dielectric system, at 45° angle of incidence.

The dispersion curves are in good agreement with the measured and modelled ATR curves shown in Figure 7.7 (c). Regarding the symmetric mode, as observed in Figure 7.7 (c), its resonance is unaffected by phonons, since their respective frequencies are found far from each other. On the other hand, the antisymmetric SPPP is clearly seen, with a fraction of reflected light close to 0 %, especially when the resonance approaches the LO sapphire phonon. In contrast, for a phonon-free dielectric substrate, the antisymmetric SPP resonance is at much lower frequencies (Figure 7.7 (b)) and thus is not detectable in the mid-IR, as simulated with the dashed lines of Figure 7.7 (c). In order to make it visible in the mid-IR, the thickest samples must be chosen, and the angle of incidence must be higher than 52°, as observed in Figure 7.8 where the modelled ATR curves of the alloys grown on a phonon-free dielectric substrate are shown.

Figure 7.8. From (a) to (e), modelled ATR curves for decreasing (Cd,Zn)O thickness and a phonon-free dielectric substrate. The angle of incidence was varied by 2° steps in the range from 39° (dark color) to 59° (light color). (f) modelled ATR curve of the bare phonon-free substrate.

However, it is worth remembering that when the (Cd,Zn)O thickness is increased, the strength of the mode is reduced, since the evanescent wave hardly reaches the (Cd,Zn)O-sapphire interface.

7.2.4. Field profiles

To confirm the existence of the symmetric and antisymmetric modes, the z -component of the electric field (E_z) at the XZ-plane in the (Cd,Zn)O film with a thickness of 65 nm was calculated, using the finite-difference time-domain (FDTD) method, from an open-source software package,¹⁷³ and it is shown in Figure 7.9. Again, in order to evaluate the effect of phonons on the LB, the E_z distribution in the air-(Cd,Zn)O-sapphire system is compared with that of an equivalent idealized system where the sapphire is substituted by the dielectric without phonons.

As observed in Figure 7.9 (a), the field distribution is antisymmetric at the frequency where the SPPP is found (1050 cm^{-1}) at 45° angle of incidence, with opposite sign in the air and sapphire half-spaces. Within the (Cd,Zn)O, E_z is close to zero, as expected for an antisymmetric mode.¹⁷⁰ When the phonons in the substrate are removed, as in Figure 7.9 (b), the antisymmetric mode is dissipated, with the plane wave being almost unaltered by

the dielectric. Besides, in agreement with Figure 7.7 (c) where the reflectance increased to 75 % at the frequency of the SPPP for a phonon-free substrate, the fraction of reflected light in Figure 7.9 (b) has also been increased since no light is absorbed by any resonance, and an interference pattern is formed in the prism.

Figure 7.9. (a) Distribution of the z-component of the electric field of a plane wave propagating along the (1,0,1) direction with a frequency of 1050 cm^{-1} , impinging at 45° on the air-(Cd,Zn)O-sapphire system, and (b) on the idealized air-(Cd,Zn)O-dielectric system. In (c), the frequency of the plane wave is 3950 cm^{-1} and it impinges on the air-(Cd,Zn)O-sapphire system. For all cases, the inset shows a zoom of the region of interest.

When the frequency of the incident light matches the resonance of the UB, the E_z distribution in Figure 7.9 (c) is formed. Now the field distribution is symmetric, with the same sign for E_z in air and in the sapphire substrate, and opposite sign within the (Cd,Zn)O thin film. When the thickness of the (Cd,Zn)O film is further reduced to 25 nm and below, this resonance approaches the ENZ mode and the E_z magnitude within the thin film is further enhanced.

7.2.5. Propagation length and field confinement distance

Once the nature of the modes has been analyzed, it is worth evaluating whether the hybridization of the oxide SPP with the sapphire SPhP improves the key field parameters of a surface mode. To answer this question, and focusing on the SPPP hybrid mode, the propagation length (L_p) along the interface and the transverse field confinement distance (δ_z) in air have been computed as a function of the frequency, solving the determinant in Eq. 7.4. The propagation length is limited by the losses in the (Cd,Zn)O and sapphire media, and therefore is inversely proportional to the imaginary part of the in-plane polariton momentum, as

$$L_p = \frac{1}{2\text{Im}\{k_x\}}. \quad (7.7)$$

The values obtained for the SPPs of the grown set of samples are compared with those of the SPPs formed in the idealized phonon-free air-(Cd,Zn)O-dielectric system and shown in Figure 7.10.

In Figure 7.10 (a), the ratio of the propagation length with and without phonons in the substrate as a function of the frequency of the incoming light is represented for every (Cd,Zn)O thickness, i.e., the propagation length of the SPPP (L_p^{SPPP}) in the air-(Cd,Zn)O-sapphire system is compared to that of the bare SPP (L_p^{SPP}) in the phonon-free air-(Cd,Zn)O-dielectric system. In order to provide a reference, the range of frequencies where the polariton can be excited in the geometry here studied is highlighted.

For a (Cd,Zn)O thickness of 150 nm, the L_p^{SPPP}/L_p^{SPP} ratio reaches a maximum of 2.9 at a frequency of 1100 cm^{-1} and then it drops for lower frequencies. This is explained as follows: considering the dispersion curve in Figure 7.7 (b) corresponding to the thickness of 150 nm, below a frequency of $\sim 1100 \text{ cm}^{-1}$ the SPP of the air-(Cd,Zn)O-dielectric system has a nearly-constant slope, being, in essence, a lossless photon propagating along the interface. In contrast, as seen in Figure 7.7 (a) for the same frequencies and thickness, the SPPP of the air-(Cd,Zn)O-sapphire system is not photon-like but phonon-plasmon-like with higher losses, explaining the drop of L_p^{SPPP} as compared to L_p^{SPP} .

Figure 7.10. (a) Ratio of the propagation length along the x-direction between the SPPP and the phonon-free SPP vs the frequency of the incoming light. Note the change in the y-scale at $y=3.1$. The inset shows the absolute values of L_p^{SPPP} and L_p^{SPP} for each sample, at the minimum measurable frequency in each case. (b) Ratio of the field confinement distance in air between the SPPP and the phonon-free SPP vs the frequency of the incoming light. The inset shows the confinement length as compared to the wavelength of the light, at the minimum measurable frequency in each case. The highlighted regions of the curves in both graphs correspond to the attainable frequencies with the ZnSe prism at an angle of incidence from 39° to 59°.

Conversely, for lower (Cd,Zn)O thicknesses the frequencies at which the dispersion curves in Figure 7.7 (b) approach the photon-line are much lower. Besides, the resonances in Figure 7.7 (a) are closer to the reststrahlen band of the sapphire phonons, and the hybrid mode acquires a phonon-like character with reduced losses. This explains the sudden rise of L_p^{SPPP} with a sapphire substrate when the frequency approaches the phonon frequencies. For a (Cd,Zn)O thickness of 65 nm, L_p^{SPPP} is 46 times L_p^{SPP} at 39° angle of incidence, and for a thickness of 25 nm the ratio is 128. Considering the absolute values shown in the inset of Figure 7.10 (a), the propagation length reaches the outstanding

values of 513 μm for the 25 nm sample and 458 μm for the 65 nm sample, much higher than the typical values for SPPs in the mid-IR. Indeed, looking at the ENZ-SPP hybrid mode observed by Runnerstrom *et al.* in a CdO system,¹⁷⁴ the propagation lengths they obtained are in the range of 5 – 40 μm in the ultra-strong coupling regime. The propagation length is one order of magnitude larger in this study, and arises from the fact that the antisymmetric mode formed in the air-(Cd,Zn)O-sapphire system does not penetrate the plasmonic material (see Figure 7.9 (a)) and so the SPPP mode suffers from lower losses than the ENZ-SPP mode. In a purely phononic structure, such as that reported by Passler for the air-AlN-SiC system,¹⁷⁵ and thanks to the reduced damping of phonons, the ENZ-SPhP hybrid mode has revealed to support a propagation length of 900 μm . However, it must be noticed that when the surface modes are entirely phononic in nature other shortcomings arise, such as the limited tunability of the resonance frequencies and the loss of confinement.

Regarding the transverse field confinement distance, which will dictate the degree of miniaturization of the components in a potential nanophotonic circuit,¹⁷⁶ it is inversely proportional to the imaginary part of the transverse component of the polariton momentum, as

$$\delta_z = \frac{1}{2\text{Im}\{k_z\}}. \quad (7.8)$$

The confinement distance of the antisymmetric SPPP mode (δ_z^{SPPP}) cannot be as low as that of ENZ-modes, where most of the field intensity lies within the plasmonic material.¹⁵⁸ As observed in Figure 7.10 (b), the ratio of the field confinement distances with and without phonons in the substrate, i.e. the ratio between δ_z^{SPPP} and the confinement distance of the bare SPP (δ_z^{SPP}), rises when the frequency is lowered, by the effect of sapphire phonons. However, its maximum value does not exceed 2 and 1.6 for the 25 nm and 65 nm (Cd,Zn)O films, respectively, which again are the thicknesses for which the hybrid SPPP mode is better formed. Thus, the gain in propagation length discussed above greatly overcomes the small loss of the confinement capability. Indeed, looking at the values in the inset of Figure 7.10 (b), the confinement distance covers the range of $(0.15 - 0.30) \lambda_0$, where λ_0 is the wavelength of the incident light, for the system without phonons, and the range of $(0.30 - 0.45) \lambda_0$ for the system with phonons. Therefore, confinement of mid-IR light is effectively achieved with the hybrid SPPP, beating the trade-off between the mode confinement and propagation present in SPPs and SPhPs.¹⁶³

7.3. Conclusion

In summary, in this work the existence of a surface plasmon-phonon polariton hybrid mode in the air-(Cd,Zn)O-sapphire system has been experimentally demonstrated, which is observable thanks to the high crystal quality of the (Cd,Zn)O films and their interface to sapphire, as well as their reduced optical losses. The coupling between the fields at the air-(Cd,Zn)O and (Cd,Zn)O-sapphire interfaces is shown to be controllable through the (Cd,Zn)O thickness, and they arrange into the symmetric mode and antisymmetric SPPP hybrid mode. Thus, through a precise control of the (Cd,Zn)O thickness and the scan of the dispersion curve by changing the angle of incidence, the frequencies where the hybrid SPPP is excited span approximately from 850 to 2500 cm^{-1} and those of the symmetric SPP mode from 3200 to 4000 cm^{-1} .

Besides, it has been shown how the SPPP hybrid mode incorporates the advantages of the bare SPP and SPhP modes. The very low damping of the sapphire phonons reduces the overall damping of the hybrid SPPP as compared to the bare SPP, especially for frequencies close to the sapphire reststrahlen band. This has a direct impact on the propagation length of the polariton, a fundamental characteristic for the employment of surface polaritons in photonic devices. For (Cd,Zn)O thicknesses of 65 nm and 25 nm, significant propagation lengths of 458 μm and 513 μm , respectively, have been obtained, i.e., one order of magnitude higher than that of typical SPPs.

Part IV

Conclusions and future work

Chapter 8. Conclusions and future work

8.1. Conclusions

In this section, the main results derived along the thesis are summarized, divided into the two covered building blocks.

8.1.1. ZnO and the (Zn,Mg)O:Ga alloy for IR intersubband-based devices

The main objective in **Chapter 4** was the analysis of the evolution of the transport and optical properties of the (Zn,Mg)O alloy, also doped with Ga, and the understanding of the concomitant presence of the Mg and Ga atoms in the wurtzite crystalline structure of ZnO. The alloys belonging to this study were grown by MBE on *m*-plane sapphire substrates, at CNRS, by the group of Assoc. Prof. Jean-Michel Chauveau. From the study, the following results and conclusions were derived.

The minimum residual electron concentration measured in the not-intentionally-doped (nid) ZnO sample was $9 \times 10^{16} \text{ cm}^{-3}$, higher than the $\sim 10^{14} \text{ cm}^{-3}$ reported in homoepitaxially-grown ZnO films, which indicates a higher concentration of donor-related defects when sapphire is used as the substrate. When doping ZnO with Ga, the measured electron concentrations matched the Ga-doping levels: for the highest Ga doping level ($4 \times 10^{19} \text{ cm}^{-3}$) an electron concentration of $4.4 \times 10^{19} \text{ cm}^{-3}$ was measured. This electron concentration caused a Burstein-Moss shift of 32 meV.

As Mg was incorporated to form the (Zn,Mg)O:Ga alloy a compensation effect was observed. The measured drop of the electron concentration was, for a nominal Ga doping level of $6 \times 10^{18} \text{ cm}^{-3}$, from $7.6 \times 10^{18} \text{ cm}^{-3}$ in ZnO to $1.5 \times 10^{18} \text{ cm}^{-3}$ when the Mg content is 20 %. For higher Mg contents the compensation effect became more evident: in the $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$ alloy, an electron concentration of $6 \times 10^{17} \text{ cm}^{-3}$ was measured for a nominal Ga content of $4 \times 10^{19} \text{ cm}^{-3}$. Despite the compensation effect arising when Mg is incorporated, for Mg contents up to 35 %, an optical electron concentration of $4.4 \times 10^{19} \text{ cm}^{-3}$ was achieved, implying a Ga doping efficiency close to 100 %.

Considering the optical and Hall electron mobilities, they were observed to decrease with the Mg content, as a result of the increase of the electron effective mass and the impurity scattering by Mg-related defects. The optical mobilities were an order of magnitude larger than the Hall mobilities due to the difference in the physics of the

technique employed: when measuring with the Hall effect technique, electrons travel microscopically and are more sensitive to extended defects as compared to the local oscillations undergone by the electrons during IR reflectance spectroscopy. Moreover, contrary to what ionized impurity-limited scattering would predict, the optical and Hall electron mobilities were observed to increase with Ga doping. This behavior was attributed to the decrease of the potential barrier formed within grain boundaries with Ga.

The growth of the (Zn,Mg)O alloy by MBE allows to achieve high Mg contents, up to 50 %, prior to phase segregation between wurtzite ZnO and cubic MgO. The high Mg contents were confirmed optically by means of UV-VIS absorption spectroscopy, revealing an optical bandgap of 4.41 eV for a Mg content of 50 % in the mid sample. The increment of the Mg content not only increases the optical bandgap, but also the Urbach tail, which moreover is independent of the Ga content and therefore can be associated to the Mg-defect-related energy states within the bandgap.

Finally, despite the observation of a blue-shift in the optical bandgap when the ZnO was highly doped with Ga, a red-shift occurs in the films with Mg, likely due to the merging of the donor miniband with the conduction band.

In **Chapter 5**, ZnO:Ga/(Zn,Mg)O heterostructures grown homoepitaxially on non-polar ZnO substrates were optically analyzed in the mid-IR, searching for the detection of the ISB absorption. Besides, quantum well infrared photodetectors were processed, and photocurrent measurements were performed on them. These are the results and conclusions from this chapter.

Intersubband transitions have been demonstrated in non-polar ZnO:Ga/(Zn,Mg)O heterostructures. Two series of samples were designed and characterized: one with varying QW thickness and another one with varying QW doping.

Regarding the former, the doping in the QW was set to $1 \times 10^{19} \text{ cm}^{-3}$, high enough to maintain populated the first bound level (the Fermi energy lies above it) and to observe ISBTs by means of IR reflectance and transmittance spectroscopies. The QW thickness was varied from 2.2 to 3.7 nm. The variation of the quantum well thickness produced a shift in the measured ISBT frequency: for the 3.7 nm-thick ZnO:Ga QWs the frequency was 1540 cm^{-1} , for 3.2 nm was 1860 cm^{-1} , for 2.7 nm was 2280 cm^{-1} and for 2.2 nm any ISBT was observed. The absence of ISB absorption in the 2.2 nm-thick QWs was likely due to

the presence of a unique bound level within the QW. The observed frequency shift was excellently reproduced by the implemented model, which accounted for the Schrödinger and Poisson equations solved self-consistently and the depolarization shift.

Considering the series with varying QW doping, the QW thickness was around 4 nm and the model predicted the formation of three bound levels. Consequently, two available ISBTs were expected. However, the coupling of the two ISBTs through the dipole-dipole interaction yielded the multisubband plasmon, a unique collective mode with its own frequency. As observed in the reflectance and transmittance experiments, although the energy position of the bound levels within the QW is almost insensitive to the doping level, the frequency of the multisubband plasmon was very sensitive to it due to the depolarization shift. Indeed, the frequency of the MSP for the lowest doped ZnO:Ga QWs ($1 \times 10^{19} \text{ cm}^{-3}$) was $\sim 2120 \text{ cm}^{-1}$, and that of the most doped ZnO:Ga QWs ($1 \times 10^{20} \text{ cm}^{-3}$) was $\sim 3950 \text{ cm}^{-1}$. Besides, as predicted by the modelling, for such high doping levels the Fermi energy exceeded the second confined level in the QW, and the absorption strength of the e_1 - e_2 transition was transferred to that of the e_2 - e_3 transition. This was confirmed by the transmittance measurements since an only e_2 - e_3 transition was observed.

The model also predicted the coupling between the electrons involved in the multisubband plasmon and the ZnO phonons, to form the intersubband polaron quasiparticle. The resonance of the intersubband polaron shifts from the frequency of the E_1 (LO) phonon of ZnO (590 cm^{-1}) to lower frequencies as the two dimensional electron concentration in the QW increases, also losing strength. However, the intersubband polaron was not experimentally confirmed.

On the other hand, QWIP structures were designed with two confined levels within the QW. In order to maximize the ISB absorption, the doping was high enough to maintain the ground level populated. The QW thickness was set to about 2.9 nm, to maintain the second confined level close to the conduction band minimum and increase the escape probability of electrons from the QW. The processing of QWIPs faced a problem arising during the wet chemical etching with diluted H_3PO_4 : deep grooves were revealed perpendicular to the c -axis of the wurtzite structure. The many attempts carried out to avoid the formation of grooves were unsatisfactory and the QWIPs were finally processed at the *Technische Universität Wien*, where the inductively coupled plasma technique was available with CH_4 , which allowed to reach the desired mesa depth in the multiple quantum wells.

The IV curves had a dark current density in the range of 1 to 0.1 A cm⁻² at 0.5 V, with a high influence of the mesa area. The trend of the current density was to increase as the mesa area of the device decreased, and therefore it was deduced that the origin of the dark current was the side-wall current. From the photocurrent results it was not possible to detect signal arising from the ISBTs, most likely due to the very high dark current of the devices.

However, in the ZOTERAC project a quantum cascade detector (QCD) was finally demonstrated in the IR, in collaboration with the *Université Paris Sud*, and the *Technische Universität Wien*.¹⁴⁶ The photovoltaic mode under the QCD works allowed to reduce the dark current and detect the ISBT photocurrent.

8.1.2. Characteristics of the (Cd,Zn)O alloy and its application to mid-IR plasmonics

In **Chapter 6**, the (Cd,Zn)O alloy was electrically and optically characterized as a function of Zn content. The maximum Zn content achievable before phase segregation, as well as the optimum Zn content of the alloy for its application as a TCO and a plasmonic material, were determined. The (Cd,Zn)O alloys were grown by MOCVD on *r*-plane sapphire substrates at *Universitat de València*. These are the main results and conclusions of the study.

From the IR reflectance measurements and modelling, the plasma frequency was observed to increase with the Zn content, indicating a rise of the free electron concentration. The damping of the plasma frequency was lower for the Cd_{0.95}Zn_{0.05}O alloy (420 cm⁻¹) than for pure CdO (577 cm⁻¹), yielding an optical electron mobility as high as 695 cm² V⁻¹ s⁻¹. For higher Zn contents the damping increased monotonically, and for 20 and 25 % Zn, a high degradation of the optical response was observed, with a damping of the plasma frequency of 875 cm⁻¹ and 934 cm⁻¹, respectively.

The transport properties of the alloy were studied by means of the Hall effect technique. The rise of the free electron concentration with the Zn content was confirmed, from 1.5 × 10²⁰ cm⁻³ in CdO to 3.9 × 10²⁰ cm⁻³ in the Cd_{0.80}Zn_{0.20}O alloy. This rise was attributed to the formation of intrinsic defects, such as hydrogen interstitials acting as single-ionized donors. The overall trend of the Hall electron mobility was similar to that observed for the optical electron mobility. For Zn contents of 5 and 10 % Hall mobilities were higher than for pure CdO, of about 110 cm² V⁻¹ s⁻¹, and contrasted the sudden

decrease reported before in polycrystalline (Cd,Zn)O films. As it happened with the optical mobility, for Zn contents of 20 and 25 % Hall mobilities were drastically reduced. These mobility results correlated with high-resolution X-ray diffraction measurements performed on the samples by Huerta-Barberà *et al.*¹⁴⁹ for Zn contents up to 10 % a single-oriented cubic crystalline orientation was detected, and for Zn contents above 20 % two crystalline structures were observed, wurtzite, from ZnO, and rock-salt, from CdO. Combining Hall mobilities and Hall electron concentrations, the resistivity of the alloy was derived, with values in the order of $\sim 10^{-4} \Omega \cdot \text{cm}$ and a minimum of $1.95 \times 10^{-4} \Omega \cdot \text{cm}$ for the $\text{Cd}_{0.90}\text{Zn}_{0.10}\text{O}$ alloy. These resistivities were found to be the lowest for the (Cd,Zn)O alloy and comparable to those from state-of-the-art highly developed CdO-based TCOs. However, it was shown that the growth temperature employed for the alloys studied in this thesis (330 °C) was lower, making the integration of the TCO in a real device easier.

In the (Cd,Zn)O alloys, the transmission window, i.e. the optical bandgap, was measured by means of UV-VIS transmission spectroscopy. The optical bandgap increased from ~ 2.6 eV in CdO to ~ 2.9 eV in the $\text{Cd}_{0.85}\text{Zn}_{0.15}\text{O}$ alloy. Considering the bandgap of CdO at Γ point is 2.17 eV, a large blue-shift was observed in all the alloys, as a result of the large electron concentrations, which induced the Burstein-Moss shift. Together with the optical bandgap, the calculated bandgap at Γ point and electron effective mass for each sample were derived, and, for pure CdO, those values matched quite well the CdO bandgap and electron effective mass given by Jefferson *et al.*²⁹ For the highest nominal Zn contents (20 and 25 %) the degradation of the crystal quality of the alloys was evident, with a reduction of the bandgap at Γ point. The electron effective mass was observed to increase with Zn content because of the conduction band non-parabolicity.

In **Chapter 7**, a detailed analysis of the hybridization of two distinct-in-nature surface modes was presented: the surface plasmon polariton, produced by (Cd,Zn)O, a plasmonic oxide, and the surface phonon polariton, produced by sapphire, a polar dielectric crystal, which also served as the substrate where the (Cd,Zn)O film was epitaxially grown. The goal was to study the characteristics of the hybrid surface plasmon-phonon polariton, looking for the enhancement of its propagation length as compared to the bare surface plasmon polariton and surface phonon polariton. From the study, the following results and conclusions were extracted.

Samples with several (Cd,Zn)O thicknesses were grown at *Universitat de València*: from 25 nm to 460 nm. The Zn content was set to 10 %, which from the previous chapter

showed to have very low optical losses in the mid-IR. By measuring attenuated total reflectance with a ZnSe prism in the Otto configuration, the surface modes of the air-(Cd,Zn)O and (Cd,Zn)O-sapphire interfaces were excited. The fields at both interfaces were observed to interact, and the interaction was analyzed as a function of the (Cd,Zn)O thickness.

In the thickest (Cd,Zn)O sample, the exponential decay of the evanescent wave within the (Cd,Zn)O made the surface mode of the (Cd,Zn)O-sapphire interface almost negligible, and the only mode observed was the surface plasmon polariton of the air-(Cd,Zn)O interface. This mode was revealed to be a pure plasmonic mode, with its corresponding asymptote for high in-plane momenta. As the thickness was reduced, the fields at both interfaces started to interact, and the surface modes were not decoupled anymore. Instead, a symmetric (higher frequencies) and an antisymmetric (lower frequencies) mode arose. For reduced (Cd,Zn)O thicknesses, the symmetric mode approached the plasma frequency, where the dielectric function of the material vanishes. Indeed, for the thinnest (Cd,Zn)O layer the mode became the so known epsilon-near-zero mode, with a symmetric field distribution, and a high field confinement.

At the same time, the dispersion curves of the antisymmetric mode shifted to lower frequencies, and the mode was revealed to be the hybrid mode formed by the surface plasmon of the (Cd,Zn)O plasmonic film and the surface phonon of the sapphire polar dielectric. Thus, the resulting hybrid mode was a surface plasmon-phonon polariton. The resonances of the antisymmetric hybrid mode were observed to be very sensitive to the (Cd,Zn)O thickness. Therefore, the nature of the mode was shown to be modulable, from a plasmon-like behavior for thicker (Cd,Zn)O films and resonances far from the sapphire phonons, to a phonon-like behavior for thinner (Cd,Zn)O films and resonances within the reststrahlen band of the E_4 sapphire phonon mode. In the ultrathin limit case, that mode was the pure surface phonon polariton of sapphire.

The focus was put on the hybrid mode, which is potentially more interesting for mid-IR plasmonic applications. The dispersion curves of the hybrid mode were computed for the different (Cd,Zn)O thicknesses, showing an excellent agreement with the measured ATR resonances as a function of the angle of incidence. These dispersion curves were compared to those computed for an idealized system where the phonons were removed from the sapphire substrate, i.e. to those from a surface plasmon polariton in a (Cd,Zn)O-dielectric interface. The range of excitable frequencies of the hybrid mode was observed to vary

substantially because of the presence of sapphire phonons, which made the surface mode more visible and easier to be controlled in the mid-IR.

Besides, the symmetry of the field of the surface modes was computed using an open-source package with the finite-difference time-domain method: the surface plasmon polariton generated at the air-(Cd,Zn)O was confirmed to be symmetric, with the electric field being enhanced within the (Cd,Zn)O plasmonic layer, while the hybrid surface plasmon-phonon polariton was confirmed to be antisymmetric, with the electric field not-penetrating in the (Cd,Zn)O.

Finally, the key parameters of the hybrid mode were analyzed: the propagation length along the interface and the confinement distance in air. In the range of frequencies where the hybrid mode was excited, the obtained propagation lengths were about one order of magnitude higher than that of typical surface plasmon polaritons, especially for thin (Cd,Zn)O films, reaching the outstanding value of 513 μm in the 25 nm-thick (Cd,Zn)O film. This enhancement of the propagation length was possible thanks to the reduced losses of the sapphire phonons, together with the fact that in the antisymmetric mode the electric field does not penetrate the (Cd,Zn)O plasmonic material, and therefore suffers from lower losses.

In contrast, it was confirmed that the confinement distance of the mode in air could not be as low as that of symmetric epsilon-near-zero modes, where most of the intensity lies within the plasmonic material. However, this loss in confinement of the hybrid mode is negligible compared to the gain in propagation length discussed above: the confinement distances in a phonon-free substrate were obtained to be about $(0.15 - 0.30) \lambda_0$, where λ_0 is the wavelength of the incident light, and a bit higher for the hybrid mode, about $(0.30 - 0.45) \lambda_0$.

8.2. Future work

The studies carried out along this thesis bring the possibility to continue with the open research lines to further investigate the capabilities of ZnO and CdO to develop devices working in the mid-IR. Thus, here some ideas are given for the next studies.

Although intersubband transitions in non-polar ZnO:Ga/(Zn,Mg)O heterostructures have been demonstrated and modelled in this thesis, further work can be carried out to develop ISB-based devices. One of the major drawbacks found in these heterostructures

is the high broadening of the ISBTs, between 800 and 1100 cm^{-1} , which would degrade the performance of future devices. The understanding of the origin of the ISB-broadening in the ZnO-based heterostructures studied in this thesis is still an issue: does it have to do with the interface roughness? May the many-body interactions contribute to it? An easy option which may give some clues about its origin may be the study of its evolution with temperature. If the broadening is reduced at low temperatures, it may have to do with the kinetic energy of the electrons in the subbands, or with the reduction of the phonon density of states.

Apart from the broadening issue, some physical phenomena can be studied in the multiple quantum well heterostructures, taking advantage of the anisotropy of the dielectric function of the material. Depending on the frequency, the sign of the dielectric function of the QWs in the direction transversal to the QW planes is different to that in the in-plane direction, as shown in Figure 8.1, where the dielectric functions have been built from Eqs. 5.5.a and 5.5.b, with an in-plane plasma frequency of 2080 cm^{-1} , a frequency for the e_1 to e_2 transition of 2500 cm^{-1} and a plasma broadening of 300 cm^{-1} .

Figure 8.1. In-plane and out-of-plane components of the dielectric function in a ZnO:Ga quantum well as a function of the frequency, built with Eqs. 5.5.a and 5.5.b and neglecting the phonon oscillators for simplicity. The in-plane plasma frequency is denoted with the vertical line at ω_p , the ISBT frequency with ω_{12} and the depolarized ISBT frequency with $\tilde{\omega}_{12}$. The colors indicate the change of sign of any of the components of the dielectric function.

The intersubband oscillator introduces a range of frequencies where the out-of-plane dielectric function is negative while the in-plane component remains positive. At the same time, the in-plane plasma frequency makes the in-plane dielectric function negative for frequencies up to the plasma frequency, while the out-of-plane component remains positive. This fact can be used to design metamaterials with a negative refraction index, as proposed by Hoffman *et al.*¹⁷⁷ where they used a multilayered InGaAs(n-doped)/AlInAs system to build the a negative refractive index metamaterial.

Other phenomena that can be studied in the multiple quantum wells is the coupling of the intersubband transitions with light-matter excitations, such as LO phonons. This has been already studied in systems such as GaAs/AlGaAs and InGaAs/AlInAs,¹⁷⁸ where the interaction of LO phonons with the ISBTs in the ultra-strong coupling regime, shows optimistic values for the polariton lasing threshold intensity, revealed to be in the order of 70 kW cm⁻².

Going a step further, when the surface plasmon polaritons couple to the intersubband transitions a new quasiparticle can be formed, as proposed by Załuźny,¹⁷⁹ the intersubband surface plasmon polariton. In his theoretical paper, the multiple quantum well active region is embedded into highly doped semiconducting claddings, which provide the surface plasmon polaritons. The hybridization of the surface mode with the intersubband transition would allow to engineer the dispersion curves of the polariton and the formation of zero-group-velocity points. The concept of coupling surface plasmons with electronic transitions in photodetectors has already been experimentally demonstrated by Lee *et al.*,¹⁸⁰ who deposited a gold pattern on top of a quantum dot infrared photodetector to enhance the detectivity of the device. Thus, they detected a thirty-fold detectivity enhancement at $\lambda = 8.1$ and $11.3 \mu\text{m}$ resulting from the coupling between the surface plasmons and the transitions in the quantum dots.

On the other hand, new designs can be tried out in plasmonic systems to exploit the benefits of the surface modes. Plasmonics in the mid-IR is a very recent topic, and during the last decades, many efforts were put on the research of new plasmonic materials with tunable plasma frequencies and reduced optical losses. Nowadays, CdO is more than a promising material and the first applications where it was implemented have emerged.¹⁵² In Chapter 7 of this thesis, plasmonic waveguides have been suggested as a possible application for the SPPP hybrid mode. To the date, there are few experimentally demonstrated plasmonic waveguides covering the mid-IR region, mainly built with metals,

where the ability of the SPPs to confine and propagate mid-IR light is enhanced with the processing of complex geometries.^{160,161} However, there are only a few theoretical proposals with doped semiconductors,^{181,182} which are more appropriate materials for the mid-IR. In this sense, the characteristics of the hybrid SPPP represent an excellent touchdown to further optimize them in more complex geometries.

The implementation of CdO in plasmonic waveguides would only be limited by the difficulty to integrate the TCO on a given substrate and by the difficulties to process the device. Fortunately, the (Cd,Zn)O alloy presented in this thesis can be deposited with temperatures as low as 300 °C. Also, it is well reported in the literature that CdO, like ZnO, is easily etchable and highly functional for different applications.¹⁶³

Among the possible applications of a plasmonic waveguide, a lab-on-chip device excels, as proposed by Schwarz *et al.*¹⁶¹ The photonics industry demands cost-effective compact devices for molecular sensing, being able to operate in remote areas where expensive and not transportable lab equipment cannot operate. Those devices could be built with three main components, as depicted in Figure 8.2.

Lab-on-chip device

Figure 8.2. Schematic of a lab-on-chip sensor composed by a quantum cascade laser, a plasmonic waveguide where the SPPP is excited, and a quantum well infrared photodetector.

First, a mid-IR laser source is required to excite the surface mode, and the best option seems to be a QCL. There are already commercial QCLs operating in the mid-IR based on GaAs, and in case further advances are achieved in the ZnO:Ga/(Zn,Mg)O heterostructures analyzed in this work (such as the mentioned reduction of the ISB broadening), ZnO-based heterostructures could take a part on it. Then, the laser source would excite a surface polariton, and here the SPPP could play an important role. With the processing of the appropriate geometry, a plasmonic waveguide can be built between the laser source and

the detector. The waveguide will transport the signal while acting as a sensor, being sensitive to the surrounding medium. To do so, light confinement and large propagation lengths would be required, and the results of the SPPP presented in Chapter 7 are promising for it. Note that, with the design of an optimized geometry for a plasmonic waveguide, the characteristics of the surface mode itself can be greatly enhanced. Finally, a detector will collect the IR light, which for instance could be a quantum well infrared photodetector.

Thus, the lab-on-chip device working in the mid-IR would be made of three main components and, in principle, all of them can be built with oxides.

Appendices

A. Intersubband polaron in ZnO:Ga/(Zn,Mg)O multiple quantum wells

Within the framework of the European ZOTERAC project, I completed a three-month stay at the Institute of Quantum Electronics of the Swiss Federal Institute of Technology (ETH) in Zurich. The purpose of the stay was the study of the intersubband polaron, a quasiparticle arising from the coupling between the electrons involved in the intersubband transitions and the LO-phonons. As discussed in Section 5.3.2, the intersubband polaron was not observed by means of IR reflectance spectroscopy, and, during the stay at the ETH, Raman spectroscopy was performed.

Figure A.1. 90° Raman geometry used for exciting the ZnO E_1 (LO) phonon. Light impinges the sample from the x-direction and is collected in the y-direction. Two polarizers (P1, P2) are used to polarize the incoming and the scattered light. The lenses (L) are used to collimate and focus the beam, as needed, and the mirrors (M) to redirect it.

The Raman set up had a laser source with an output of 6 mW emitting at 532.1 nm (2.33 eV), so band-to-band transitions were not excited (recall ZnO bandgap is 3.37 eV). A spectrometer together with a CCD detector were used to collect the scattered signal. The

peculiarity of the E_1 (LO) phonon of the wurtzite structure is that, due to the Raman selection rules, it can only be excited in a 90° geometry,¹⁸³ as depicted in Figure A.1.

The Raman set up at ETH was prepared for measuring in a backscattering geometry, so first the work of the PhD student was to optimize the 90° geometry to maximize the signal in the detector. According to the Porto notation, this configuration can correspond to the $x(yz)y$ and $x(zx)y$ scattering geometries, depending on the light polarization. In the Porto notation, the first and the last letters indicate the direction of the incident and scattered light, respectively, and the first and second letters in brackets the direction of the polarization of the incident and scattered light, respectively. Lens 3 (L3 in Figure A.1) was used to focus the light in a tiny spot of $\sim 2 \mu\text{m}$ in diameter.

First, and in order to have a reference of the observable phonon modes, a ZnO substrate was measured in the 90° geometry and also in the backscattering geometry, and the recorded spectra are shown in Figure A.2.

Figure A.2. Raman spectra of a ZnO substrate for different geometries. Following the study of Cuscó *et al.*,¹⁸⁴ the axial (A) or planar (E) symmetries are indicated in each observed peak.

As observed, the E_1 (LO) phonon is most visible in the $x(yz)y$ geometry (green line in Figure A.2), in agreement with the Raman selection rules. The peaks appearing for the different geometries are associated to the planar (E) or axial (A) symmetries, as in Cuscó *et al.*¹⁸⁴ In order to investigate the intersubband polaron, the samples in Section 5.3.2 with

a QW thickness of about 4 nm and varying Ga doping levels, as well as two extra samples with lower doping levels specifically designed for this study, were measured by Raman spectroscopy. As an example, a Raman scan in the x-direction of a sample with a doping level in the QW of $2 \times 10^{18} \text{ cm}^{-3}$ is shown in Figure A.3.

Figure A.3. Raman scan in the x-direction and in the $x(yz)y$ geometry of a sample with a quantum well thickness of 4 nm and a doping level of $2 \times 10^{18} \text{ cm}^{-3}$.

In all the measurements, the signal from the substrate was so high that the signal arising from the multiple quantum wells was not observed. The polaron was not detected, but neither were the phonon modes of the (Zn,Mg)O barriers (their frequencies were shown in Figure 4.7). Likely, the spot diameter ($\sim 2 \mu\text{m}$) is too big compared to the active region ($\sim 400 \text{ nm}$) and most of the signal originates from the ZnO substrate. This is the reason why the scan was made, to try to find the x-position which maximizes the signal from the active region.

The many attempts done in this and the other samples did not result in satisfactory results, i.e. in the observation of the intersubband polaron. The growth of the multiple quantum well heterostructures in sapphire substrates to avoid the signal from the ZnO substrate, and the use of the resonant Raman scattering technique (for instance with a HeCd laser source emitting at 325 nm, or 3.8 eV) may help in future experiments for the search of this quasiparticle.

B. Bulk vs interface light-matter polaritons in polar semiconductors

In this appendix, the nature of the light-matter excitations in polar semiconductors is discussed. In the literature, it is usual to refer indistinctly to bulk and interface modes, and the useless of a unique and concise nomenclature hinders the understanding of the physics behind the phenomena.

With the aim of clarifying the nature and the nomenclature of the light-matter excitations appearing along this thesis, here the arising polaritons in a polar semiconductor with a pair of TO-LO phonons will be shown. The approach can be also implemented in a similar way in a medium with other light-matter excitations, such as plasmons or intersubband transitions.

As indicated in Chapter 4, to model the reflectance curves of a pair of TO-LO phonons, the dielectric function of the material is represented by the oscillator

$$\varepsilon(\omega) = \varepsilon_{\infty} \frac{\omega_{LO}^2 - \omega^2 - i\omega\gamma_{LO}}{\omega_{TO}^2 - \omega^2 - i\omega\gamma_{TO}}. \quad (B.1)$$

From Eq. B.1 and setting $\omega = 0$, it is straightforward to obtain the Lyddane-Sachs-Teller relation

$$\frac{\varepsilon_0}{\varepsilon_{\infty}} = \frac{\omega_{LO}^2}{\omega_{TO}^2}. \quad (B.2)$$

For the calculations in this appendix, the following numbers of a hypothetical phonon oscillator have been used:

ε_0	ε_{∞}	$\omega_{TO} \text{ (cm}^{-1}\text{)}$	$\gamma_{TO} \text{ (cm}^{-1}\text{)}$	$\omega_{LO} \text{ (cm}^{-1}\text{)}$	$\gamma_{LO} \text{ (cm}^{-1}\text{)}$
5.88	3	500	15 and 0	700	15 and 0

Table B.1. Values used for the phonon oscillator.

The real and imaginary parts of the dielectric function in Eq. B.1 with the numbers above are represented in Figure B.1 (a). As observed, for low frequencies the real part tends to ε_0 and for high frequencies it tends to ε_{∞} . At ω_{TO} the real part changes its sign, from positive values below it to negative values above it. Also, at ω_{TO} the imaginary part

(related with the losses of the oscillator) has its maximum value. Between ω_{TO} and ω_{LO} the real part of the dielectric function is negative: this is the reststrahlen band of the phonon pair and, in that range, light cannot propagate within the bulk material. In Figure B.1 (b) a lossless material has been considered, i.e. with $\gamma_{TO,LO} = 0$. Note that, in such undamped oscillator, the imaginary part becomes zero and the real part has an asymptote at ω_{TO} .

Figure B.1. Real and imaginary parts of the dielectric function for the TO-LO oscillator described by Eq. B.1 and using the values in Table B.1, (a) for a damped oscillator and (b), setting $\gamma_{TO,LO} = 0$.

Bulk modes

It is well known that the dispersion of light in an infinite medium with a dielectric function $\varepsilon(\omega)$ is given by

$$k = \omega \sqrt{\varepsilon(\omega)}, \quad (\text{B.3})$$

where k stands for the momentum of the electromagnetic wave propagating in the $(k_x, k_y, k_z) = (\sin \theta, 0, \cos \theta)$ direction, as

$$k = \sqrt{k_x^2 + k_z^2} = \sqrt{(k \sin \theta)^2 + (k \cos \theta)^2}. \quad (\text{B.4})$$

For convenience, the speed of light factor has been set to $c = 1$. Also, for simplicity in the calculations, the lossless oscillator in Figure B.1 (b) has been considered in the remainder of the appendix.

Actually, it does not make sense to talk about bulk polaritons in an infinite medium, just because such infinite medium does not exist. However, bulk polaritons can be excited when light impinges a semi-infinite medium from a different one. Therefore, an s-polarized electromagnetic wave propagating in air and impinging at the semi-infinite medium described by Eq. B.1 at an angle of incidence θ is considered, as schematized in Figure B.2. Since light is s-polarized, the electric field is parallel to the interface and does not “see” it, i.e., only the bulk modes will be excited.

Figure B.2. s-polarized light impinging from air to the medium with phonons described by Eq. B.1 at an angle of incidence θ .

From Eqs. B.1 and B.3 it is clear that, for each ω value, there will be two possible solutions for k . The dispersion relation is shown in Figure B.3.

Figure B.3. Dispersion relation of a bulk polariton. The green dotted lines indicate the asymptotes of the upper and lower branches, with slopes $1/\sqrt{\epsilon_\infty}$ and $1/\sqrt{\epsilon_0}$, respectively, and the red dotted line the light dispersion in air. The crossing frequency between the upper branch of the bulk polariton and the light line is indicated. The reststrahlen band formed between the TO and LO phonons is shaded in green.

The blue lines represent the upper and lower branches of the bulk phonon polariton. As observed, it has no resonances within the reststrahlen band formed by phonons. Besides, from Eq. B.3, it can be easily deduced that the slope at which the lower branch tends for lower frequencies is $1/\sqrt{\epsilon_0}$, and, similarly, the slope at which the upper branch tends for high frequencies is $1/\sqrt{\epsilon_\infty}$. It is worth to note that, since the electromagnetic wave is transverse, with the electric field perpendicular to the direction of propagation of the wave, it cannot be coupled to LO phonons, since their momentum is parallel to the electric field. Thus, the nature of the two branches is transverse. The light line in air is represented by the red dotted line, with slope equal to 1. The momentum of light must be conserved, and therefore, the crossing point between the light line in air and the upper branch of the bulk phonon polariton is the only resonance excitable. As a result, in the s-polarized reflectance spectrum, it appears a reflectance minimum at that frequency (781 cm^{-1}), as was modelled with the TMM and shown in Figure B.4.

Figure B.4. *s*-polarized reflectance spectra for the system in Figure B.2, at 50° angle of incidence. Note the logarithmic scale. The grey dotted lines indicate the frequencies of the TO and LO phonons, and the red dotted line the resonance of the bulk phonon polariton.

Interface modes

The discussion about the bulk modes has been illustrated with an *s*-polarized light impinging in a semi-infinite medium with phonons, but what if light is *p*-polarized? As shown in Figure B.5, in *p*-polarization the electric field has a component parallel and a component transversal to the interface between the two media. Thus, the transversal component of the electric field will “see” the interface and will excite different modes, here referred to interface modes.

Figure B.5. (a) *p*-polarized light impinging from air to the medium with phonons described by Eq. B.1 at an angle of incidence θ .

Now, as described in Section 2.5.2, by applying the boundary conditions at the interface to each of the components of the electric and magnetic fields, the following dispersion relation is obtained

$$k_x = \omega \sqrt{\frac{\varepsilon_1 \varepsilon_2(\omega)}{\varepsilon_1 + \varepsilon_2(\omega)}}, \quad (\text{B.5})$$

where, in the system of Figure B.5, ε_1 stands for the air dielectric constant (i.e. $\varepsilon_1 = 1$), and $\varepsilon_2(\omega)$ for the lossless phonon oscillator. The difference with respect to the bulk modes is that now, since the symmetry is broken at the interface and the momentum and electric field are decomposed into their x and z components, their relative weight can be changed with the angle of incidence θ . The resulting dispersion curve is represented in Figure B.6.

Figure B.6. (a) Dispersion curve of the interface phonon polariton of the system depicted in Figure B.5. The blue solid lines are the Brewster modes and the green solid line the Fano mode. The blue shaded region falls above the light line (red dotted line) and the red shaded region below it. The black curved arrow indicates the region excitable with the coupling of a prism in the Otto configuration, with a refractive index n_{prism} and at an angle of incidence from 90° to 0° . The reststrahlen band formed by the TO-LO phonons is shaded in green. (b) 1: slope of the asymptote of the Brewster mode for high frequencies; 2: slope of the asymptote of the Brewster mode for low frequencies; 3: light line in air; 4: light line in a prism with a refractive index n_{prism} ; 5: asymptote of the Fano mode for high in-plane momenta.

Concerning the blue curves in Figure B.6 (a), that mode is commonly known as the Brewster mode: for each frequency of the polariton, its corresponding Brewster angle of

incidence and therefore k_x has to be chosen in order to excite it. As observed, the light line crosses the lower branch at ω_{TO} and divides it into the Brewster mode and the surface mode. The Brewster mode falls at the left of the light line and therefore is excitable without a prism. In the literature is also known as the radiative mode, since it is not bound to the interface and can leak into air.

From Figure B.6 (a) it is clear that for exciting the Fano mode, which falls at the right of the light line, a prism with a high refractive index has to be employed, with a light line represented by the orange dotted line. With the prism, the momentum of the electromagnetic wave is matched with that of the surface polariton. The Fano mode corresponds to the surface phonon polariton propagating along the interface of the two media (note the difference between interface and surface mode in this appendix), and to such sort of modes belongs the hybrid mode studied in Chapter 7.

Besides, note the following differences of the interface modes in Figure B.6 with respect to the bulk modes in Figure B.3:

- In contrast to the bulk modes, where the asymptotes depend on the high-frequency and low-frequency dielectric constants of the bulk material, the interface modes have different asymptotes, which depend on both media, with slopes 1 and 2 in Figure B.6 (b).
- For the bulk polariton the dispersion curve is represented in a ω vs k graph while the interface polariton is represented in a ω vs k_x graph. Therefore, the in-plane momenta of the interface polariton can be scanned with the angle of incidence, since $k_x = k \sin \theta$.
- Related with the previous point, for the bulk modes the slope of the light line is larger than the slope of the two asymptotes of the material, and, at the crossing point with the bulk polariton, the resonance appears in the reflectance spectra. In the interface modes, the slope of the light line is lower than that of the asymptotes of the interface polariton branches, and therefore, by changing the angle of incidence, both branches can be excited.
- Due to the conservation of momentum, bulk modes are purely transversal. However, in p -polarization the deconvolution of the electric field and momentum in their x - and z -components produces that, at the interface, $E_x \parallel k_x$ and $E_z \parallel k_z$, and longitudinal optical oscillations can be excited. These longitudinal optical

oscillations produce a dipole at the interface which results in a sharp minimum in the reflectance spectra: the interface or Brewster mode.

Finally, the p -polarized reflectance spectrum of the system has been calculated and it is shown in Figure B.7. The same resonance than that obtained in s -polarization at 781 cm^{-1} , corresponding to the bulk polariton, can be observed. The in-plane component of the electric field in p -polarization is exciting it, and it is invariable with the angle. In addition, the interface mode arises at a higher frequency, and it is excited by the out-of-plane component of the electric field. This is the Brewster mode and it shifts to higher frequencies as the in-plane momenta increases, i.e. as the angle of incidence increases, following the dispersion curve in Figure B.6 (a).

Figure B.7. p -polarized reflectance spectra for the system in Figure B.5, at 50° angle of incidence. Note the logarithmic scale. The grey dotted lines indicate the frequencies of the TO and LO phonons, the red dotted line the resonance of the bulk polariton, and the blue dotted line the resonance of the interface polariton.

Along the thesis, most of the reflectance spectra correspond to p -polarization, since their associated interface resonances produce sharper minimums in the spectra, and it is easier to model them. Note that in this appendix, the modelled reflectance curves are presented in logarithmic scale, which facilitates the observation of the bulk modes which otherwise would be hidden by the interface modes with sharper minimum peaks. Besides, the oscillators modelled in this thesis have finite losses, and the damping reduces the visibility of the modes. Also, some light-matter excitations such as the intersubband

transitions in Chapter 5 and the surface modes in Chapter 7 are only excitable when a component of the electric field is transversal to the interface, i.e. in p -polarization.

C. List of publications and conference contributions

Peer-reviewed journal publications

- (1) **J. Tamayo-Arriola**, M. Montes Bajo, N. Le Biavan, D. Lefebvre, A. Kurtz, J. M. Ulloa, J.-M. Chauveau, A. Hierro, "Ga-doping of nonpolar m-plane ZnMgO with high Mg contents," *J. Alloy. Compd.* 766, 436-441, 2018.
- (2) **J. Tamayo-Arriola**, A. Huerta-Barberà, M. Montes Bajo, E. Muñoz, V. Muñoz-Sanjosé, A. Hierro, "Rock-salt CdZnO as a transparent conductive oxide," *Appl. Phys. Lett.* 113, 222101, 2018.
- (3) **J. Tamayo-Arriola**, E. Martínez Castellano, M. Montes Bajo, A. Huerta-Barberà, E. Muñoz, V. Muñoz-Sanjosé, A. Hierro, "A Controllable and Highly Propagative Hybrid Surface Plasmon-Phonon Polariton in a CdZnO-based Two-Interface System," *ACS Photonics*, accepted, september 2019.
- (4) M. Montes Bajo, **J. Tamayo-Arriola**, M. Hugues, J. M. Ulloa, N. Le Biavan, R. Peretti, F. H. Julien, J. Faist, J.-M. Chauveau, A. Hierro, "Multisubband Plasmons in Doped ZnO Quantum Wells," *Phys. Rev. Applied*, 10, 024005, 2018.
- (5) M. Montes Bajo, **J. Tamayo-Arriola**, N. Le Biavan, J. M. Ulloa, P. Vennégues, D. Lefebvre, M. Hugues, J.-M. Chauveau, A. Hierro, "Breaking the Intersubband Selection Rules for Absorption with ZnO Quantum Wells: Light Polarization Sensitivity under Normal Incidence," *Phys. Rev. Applied*, 10, 034022, 2018.
- (6) A. Hierro, M. Montes Bajo, M. Ferraro, **J. Tamayo-Arriola**, N. Le Biavan, M. Hugues, J. M. Ulloa, M. Giudici, J.-M. Chauveau, P. Genevet "Optical phase transition in semiconductor quantum metamaterials," *Phys. Rev. Lett.* 123, 117401, 2019.
- (7) N. Le Biavan, M. Hughes, M. Montes Bajo, **J. Tamayo-Arriola**, A. Jollivet, D. Lefebvre, Y. Cordier, B. Vinter, F. H. Julien, A. Hierro, J.-M. Chauveau, "Homoepitaxy of non-polar ZnO/(Zn,Mg)O multi-quantum wells: From a precise growth control to the observation of intersubband transitions," *Appl. Phys. Lett.* 111, 231903, 2017.

- (8) A. Huerta-Barberà, L. M. Guia, O. Klymov, V. Marín-Borrás, C. Martínez-Tomás, **J. Tamayo-Arriola**, A. Kurtz, M. Montes Bajo, E. Muñoz, A. Hierro, and V. Muñoz-Sanjosé, "MOCVD growth of CdO very thin films: Problems and ways of solution," *Appl. Surf. Sci.* 385, 209–215, 2016.
- (9) A. Jollivet, B. Hinkov, S. Pirotta, H. Hoang, S. Derelle, J. Jaeck, M. Tchernycheva, R. Colombelli, A. Bousseksou, M. Hugues, N. Le Biavan, **J. Tamayo-Arriola**, M. Montes Bajo, L. Rigutti, A. Hierro, G. Strasser, J.-M. Chauveau, and F. H. Julien, "Short infrared wavelength quantum cascade detectors based on m-plane ZnO/ZnMgO quantum wells," *Appl. Phys. Lett.* 113, 251104, 2018.

Peer-reviewed proceeding publications

- (1) M. Montes Bajo, **J. Tamayo-Arriola**, J. M. Ulloa, A. Jollivet, M. Tchernycheva, F. H. Julien, R. Peretti, J. Faist, M. Hugues, J.-M. Chauveau, A. Hierro, "Intersubband absorption in m-plane ZnO/ZnMgO MQWs," *SPIE Proceedings, Oxide-based Materials and Devices VIII*, 10105, 2017.
- (2) M. Montes Bajo, **J. Tamayo-Arriola**, N. Le Biavan, J. M. Ulloa, P. Vennéguès, D. Lefebvre, M. Hugues, J.-M. Chauveau, A. Hierro, "Intersubband absorption at normal incidence by m-plane ZnO/MgZnO Quantum Wells," *SPIE Proceedings, Oxide-based Materials and Devices X*, 10919, 2019.
- (3) A. Hierro, M. Montes Bajo, **J. Tamayo-Arriola**, M. Hugues, R. Peretti, F. H. Julien, J. Faist, J.-M. Chauveau, "Intersubband transitions and many body effects in ZnMgO/ZnO quantum wells," *SPIE Proceedings, Oxide-based Materials and Devices IX*, 10533, 2018.
- (4) M. Ferraro, M. Giudici, A. Vasanelli, M. Montes Bajo, **J. Tamayo-Arriola**, A. Hierro, J.-M. Chauveau, P. Genevet, "Intersubband plasmons induced negative refraction at mid-IR frequency in heterostructured semiconductor metamaterials," *Journal of Physics: Conference Series*, 1092, 012034, 2018.

Invited oral presentations

- (1) M. Montes Bajo, N. Le Biavan, **J. Tamayo-Arriola**, A. Torres-Pardo, J. M. González-Calvet, J. M. Ulloa, D. Lefebvre, M. Hugues, J.-M. Chauveau, and A. Hierro,

- "Breakage of the polarization selection rules for intersubband transitions in ZnO/MgZnO quantum wells," *SPIE Photonics West*, San Francisco, United States, 2018.
- (2) M. Montes Bajo, **J. Tamayo-Arriola**, J. M. Ulloa, A. Jollivet, N. Isac, A. Bousseksou, M. Tchernycheva, F. H. Julien, R. Peretti, J. Faist, N. Le Biavan, M. Hugues, J.-M. Chauveau, and A. Hierro, "Mid-IR intersubband absorption in m-plane ZnO/ZnMgO MQWs," *SPIE Photonics West*, San Francisco, United States, 2017.
- (3) J.-M. Chauveau, M. Hugues, N. Le Biavan, D. Lefebvre, M. Montes Bajo, **J. Tamayo-Arriola**, A. Hierro, P. Quach, A. Jollivet, N. Isac, A. Bousseksou, M. Tchernycheva, F. H. Julien, B. Hinkov, G. Strasser, R. Peretti, G. Scalari, and J. Faist, "Non-polar ZnO/(Zn,Mg)O heterostructures for intersubband devices: novel applications with an old material system?," *SPIE Photonics West*, San Francisco, United States, 2017.
- (4) A. Hierro, M. Montes Bajo, **J. Tamayo-Arriola**, M. Hugues, J. M. Ulloa, N. Le Biavan, R. Peretti, F. H. Julien, J. Faist, J.-M. Chauveau, "Phonon-intersubband transition coupling in MgZnO/ZnO quantum wells," *SPIE Photonics West*, San Francisco, United States, 2018.
- (5) J.-M. Chauveau, N. Le Biavan, M. Hugues, M. Montes Bajo, **J. Tamayo-Arriola**, A. Jollivet, B. Hinkov, B. Meng, D. Lefebvre, Y. Cordier, F. H. Julien, A. Hierro, G. Strasser, J. Faist, "Homoepitaxy of non-polar ZnO/(Zn,Mg)O multi-quantum wells: from a precise growth control to the observation of intersubband transitions," *SPIE Photonics West*, San Francisco, United States, 2018.
- (6) M. Hugues, N. Le Biavan, D. Lefebvre, M. Montes Bajo, **J. Tamayo-Arriola**, A. Hierro, A. Jollivet, M. Tchernycheva, F. H. Julien, J.-M. Chauveau, "ZnO: from material to unipolar devices," *SPIE Optics + Photonics*, San Diego, United States, 2017.
- (7) M. Montes Bajo, **J. Tamayo-Arriola**, J. M. Ulloa, N. Le Biavan, M. Hugues, J.-M. Chauveau, A. Hierro, "Interface phonon-polaritons as an all-optical technique to assess the Mg content in ZnO/MgZnO multiple quantum wells," *SPIE Photonics West*, San Francisco, United States, 2019.

- (8) A. Hierro, M. Montes Bajo, **J. Tamayo-Arriola**, J. M. Ulloa, N. Le Biavan, D. Lefebvre, M. Hugues, J.-M. Chauveau, "Using ZnO multiple quantum well metastructures for IR light polarization sensitive photodetection under normal incidence," *SPIE Photonics West*, San Francisco, United States, 2019.
- (9) J.-M. Chauveau, M. Ferraro, M. Montes Bajo, **J. Tamayo-Arriola**, N. Le Biavan, M. Hugues, M. Giudici, A. Vasanelli, P. Genevet, A. Hierro, "Intersubband transitions in wide band gap semiconductor oxides: a tool to tune the hyperbolic response in metamaterials," *SPIE Photonics West*, San Francisco, United States, 2019.
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Regular oral presentations

- (1) **J. Tamayo-Arriola**, A. Huerta-Barberà, M. Montes Bajo, E. Muñoz, V. Muñoz-Sanjosé, A. Hierro, "Bandgap energy and electrical properties of cubic $\text{Cd}_{1-x}\text{Zn}_x\text{O}$," *10th International Workshop on Zinc Oxide and Other Oxide Semiconductors*, Warsaw, Poland, 2018.
- (2) **J. Tamayo-Arriola**, M. Montes Bajo, D. Lefebvre, N. Le Biavan, M. Hugues, J. M. Ulloa, J. M. Chauveau, A. Hierro, "Electrical and transport characteristics of non-polar m-plane $\text{Ga:Mg}_x\text{Zn}_{1-x}\text{O}$," *European-Material Research Society*, Warsaw, Poland, 2017.
- (3) E. Martínez Castellano, **J. Tamayo-Arriola**, M. Montes Bajo, A. Huerta-Barberà, E. Muñoz, V. Muñoz-Sanjosé, A. Hierro, "Double-interface surface plasmon modes in CdZnO thin films and their hybridization with phonons" *The 10th International Conference on Metamaterials, Photonic Crystals and Plasmonics*, Lisbon, Portugal, 2019.
- (4) M. Montes Bajo, **J. Tamayo-Arriola**, J. M. Ulloa, A. Jollivet, F. H. Julien, R. Peretti, G. Scalari, J. Faist, N. Le Biavan, M. Hugues, J. M. Chauveau, and A. Hierro, "Infrared

- intersubband absorption from non-polar homoepitaxial m-ZnO/ZnMgO MQWs," *The 9th International Workshop on Zinc Oxide*, Taipei, Taiwan, 2016.
- (5) A. Hierro, M. Montes Bajo, **J. Tamayo-Arriola**, J.M. Ulloa, N. Le Biavan, M. Hugues, J.M. Chauveau, "Interfacial phonon resonances in ZnO/MgZnO quantum wells: a compositional calibration tool," *10th International Workshop on Zinc Oxide and Other Oxide Semiconductors*, Warsaw, Poland, 2018.
- (6) N. Le Biavan, M. Hugues, M. Montes Bajo, **J. Tamayo-Arriola**, A. Jollivet, D. Lefebvre, Y. Cordier, B. Vinter, F. H. Julien, A. Hierro, J.-M. Chauveau, "Homoepitaxy on non-polar ZnO/(Zn, Mg)O multi-quantum wells: From a precise growth control to the observation of intersubband transitions," *10th International Workshop on Zinc Oxide and Other Oxide Semiconductors*, Warsaw, Poland, 2018.
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- (10) M. Ferraro, M. Giudici, A. Vasanelli, M. Montes Bajo, **J. Tamayo-Arriola**, A. Hierro, J.-M. Chauveau, P. Genevet, "Intersubband plasmons induced negative refraction at mid-IR frequency in heterostructured semiconductor metamaterials," *International Conference on Metamaterials and Nanophotonics*, Sochi, Russia, 2018.

- (11) M. Ferraro, M. Montes Bajo, **J. Tamayo-Arriola**, M. Giudici, A. Vasanelli, J.-M. Chauveau, A. Hierro, P. Genevet, "Intersubband plasmons induced negative refraction at mid-IR frequency in heterostructured semiconductor metamaterials," *Nanophotonics and Micro/Nano Optics International Conference*, Rome, Italy, 2018.
- (12) J.-M. Chauveau, M. Hugues, N. Le Biavan, F. H. Julien, R. Peretti, J. Faist, M. Montes Bajo, **J. Tamayo-Arriola**, J. M. Ulloa, A. Hierro, "Intersubband Transitions and Polarons in (Zn,Mg)O/ZnO Quantum Wells," *14th International Conference on Intersubband Transitions in Quantum Wells*, Marina Bay Sands, Singapore, 2017.
- (13) J.-M. Chauveau, M. Hugues, N. Le Biavan, F. H. Julien, R. Peretti, J. Faist, M. Montes Bajo, **J. Tamayo-Arriola**, J. M. Ulloa, A. Hierro, "MBE Growth of Polar, Nonpolar and semipolar (Zn,Mg)O/ZnO for potential UV and THz applications," *Austrian MBE Workshop*, TU Wien, Austria, 2017.

Poster presentations

- (1) **J. Tamayo-Arriola**, E. Martínez Castellano, A. Huerta-Barberà, M. Montes Bajo, E. Muñoz, V. Muñoz-Sanjósé, A. Hierro, "Rock-salt CdZnO for IR plasmonics" *The 10th International Conference on Metamaterials, Photonic Crystals and Plasmonics*, Lisbon, Portugal, 2019.

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