Structural and electrical properties of Co-doped ZnO prepared by DC-Magnetron co-sputtering for spintronic applications

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Universidad Nacional de Colombia
Science Faculty, Physics Department
Bogotá, Colombia
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Sanity and happiness are an impossible combination.

Mark Twain

To my parents.
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In memory of my grandpa, who I know is proud of me, wherever he is.
Abstract

In this work, the effect of Cobalt in $ZnO$ thin films was studied. The samples were synthesized by DC-Magnetron co-sputtering over different substrates (Glass, $Al_2O_3$, ITO, $Si$, and $Au$). Structural and electrical properties were studied through several characterization techniques, correlating the synthesis parameters and varying them until an optimal semiconductor matrix was achieved. Looking for the best configuration for a spintronic device, these and other characteristics of the samples were studied using diverse techniques, such as scanning electron microscopy, Auger spectroscopy, X-ray diffraction, atomic force microscopy, energy-dispersive X-ray spectroscopy, ultraviolet-visible-near-infrared spectroscopy, electric measurements (Resistance and current-voltage curves) and magnetization measurements. Additionally, a computational study of the oxygen vacancies and cobalt role in the room-ferromagnetism was performed. This approach was based on the density functional theory, where different configurations of impurities were analyzed. A room temperature ferromagnetic stability was predicted in the $Zn_xCo_{1-x}O_y$ structure, also a decrease in the magnetic moment was founded when the oxygen vacancies increased. Experimentally, the Cobalt concentration in the samples was determined and secondary phases of Cobalt were not found in concentrations below 15%, and the d-d bond was confirmed by optical measurements. The thickness of the thin films was between 50 and 190 nm, with Zinc:Oxygen in a 2:1 proportion. On the surface of the samples, the roughness increased with the cobalt concentration, and the samples with $\sim$ 15% presented a superficial magnetic orientation. The application as non-volatile memory was studied, current-voltage measurements showed the resistive switching phenomenon reported for the pure semiconductor, with a strong correlation with the Cobalt. The switching was performed with different limit currents and, the reliability and durability of the device were tested. The samples’ magnetization exhibited hysteresis loops at room temperature when the samples have a considerable crystallinity. The magnetic behavior at room temperature along with the interesting electric properties brings the $Co:ZnO$ thin films prepared by DC-magnetron co-sputtering as a possible spintronic material for electronic applications.

Keywords: $ZnO$, room-temperature ferromagnetism, resistive switching, non-volatile memories, Cobalt.
Resumen

En este trabajo se estudió el efecto del cobalto en películas delgadas de ZnO. Las muestras se sintetizaron mediante pulverización catódica sobre diferentes sustratos (vidrio, Al₂O₃, ITO, Si y Au). Las propiedades estructurales y eléctricas fueron estudiadas, correlacionando los parámetros de síntesis y variándolos hasta lograr un semiconductor óptimo. Con la aplicación espintrónica en mente, se estudiaron estas y otras características de las muestras utilizando diversas técnicas, como microscopía electrónica de barrido, espectroscopía Auger, difracción de rayos X, microscopía de fuerza atómica, espectroscopía de rayos X de energía dispersiva, foto-espectroscopía, medidas eléctricas (resistencia y curvas de corriente-voltaje) y medidas de magnetización. Además, se realizó un estudio computacional sobre el papel de las vacancias de oxígeno y el cobalto en el ferromagnetismo a temperatura ambiente. Este enfoque se basó en la teoría funcional de la densidad, donde se analizaron diferentes configuraciones de impurezas y se predijo una estabilidad ferromagnética a temperatura ambiente. Experimentalmente, se determinó la concentración de cobalto en las muestras y no se encontraron fases secundarias en concentraciones por debajo del 15 %. La presencia del enlace d-d se confirmó mediante mediciones ópticas de las películas delgadas, cuyo espesor varió entre 50 y 190 nm, con una proporción entre Zinc: Oxígeno de 2: 1. En la superficie de las muestras, la rugosidad aumentó con la concentración de cobalto, y las muestras con sim 15 % presentaron una orientación magnética superficial. Las medidas de corriente-voltaje mostraron el fenómeno de conmutación resistiva reportado para el semiconductor puro, con una fuerte correlación con el cobalto. La conmutación se realizó con diferentes corrientes límite, donde la confiabilidad y durabilidad del dispositivo fue comprobada. La magnetización de las muestras exhibió histéresis a temperatura ambiente en las muestras con cristalinidad considerable. El comportamiento magnético a temperatura ambiente junto con las interesantes propiedades eléctricas hace que las películas delgadas de Co : ZnO preparadas mediante pulverización catódica sean un posible material con aplicaciones en la espintrónica.

Palabras clave: ZnO, ferromagnetismo, conmutación resistiva, memorias no volátiles, cobalto.
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1. Introduction

The modern era has brought along with technological innovations the need to handle enormous amounts of digital data \[1\]. Every day the humanity creates 2.5 quintillion bytes of data \[2\]. This would fill 10 million Blu-ray discs, the height of which stacked would measure the height of four Eiffel Towers one top another. That information needs to be processed, stored, and analyzed at high speeds; in 2013 global internet traffic was approximately 51 billion gigabytes, in 2018 grew to 50 000 GB per second, and today the number of people who have access to the internet equals that of the world population in 1960 (3 billion) \[2\]. In this context, velocity is defined as the increasing speed at which data is created and the speed at which it can be processed, stored and analyzed. Analyzing that information is a challenge for the current coding, due to the lack of data structure, the growing social need for privacy and encryption, and the enormous number of sources and access routes that request the information simultaneously.

Trying to overcome the limitations of the current coding, the scientific community has turned to develop devices that can support the growth of information, which currently has a growth equal to four times the world economy \[2\]. In particular, the challenge of storage and data processing devices is to deal with information avalanches, preserving or even improving high velocity, with high data density, low power consumption, high durability, and low market prices \[3\][4]. In this sense, spintronics was born as a hope to take humanity to the next level of information and data processing \[5\]. The spin could be stored in semiconductors, run at frequencies many times faster than today’s technology, and work at room temperature; all in a single nanostructure \[6\].

Spintronics (a portmanteau meaning spin transport electronics), also known as spin electronics, is the study of the intrinsic spin of the electron and its associated magnetic moment, in addition to its fundamental electric charge, in solid-state devices \[7\]. Spintronics emerged from discoveries in the 1980s concerning spin-dependent electron transport phenomena in solid-state devices \[8\]. The first mass-produced spintronic device has already revolutionized the hard-disk drive industry. Introduced in 1997, the giant magneto-resistive (GMR) head, developed at the IBM Almaden lab, is a super-sensitive magnetic-field sensor that enabled a 40-fold increase in data density over the past seven years \[9\]. The first use of spin-valve sensors in hard disk drive read heads was in the IBM Deskstar 16GP Titan, which was released in 1997 with 16.8 GB of storage \[10\]. In 2007, Hitachi, which bought IBM’s hard drive
division in 2003, released the Deskstar 7K1000, the first 1 TB hard disk drive [11]. Today, the Hitachi Deskstar 7K3000 provides up to 3 TB of storage [12]. Another multilayered spintronic structure is at the heart of the high-speed, nonvolatile magnetic random-access memory (MRAM), currently being developed by a handful of companies [6,13].

One of the proposals that has revolutionized the way of understanding solid matter physics as we know it, and has come close enough to the dreamed electronics, are the spintronic devices. A spintronic device is a system based on materials that take advantage of both the electrical and magnetic properties of the electron, which is considered the fundamental particle in electronic processes. The idea of these devices is to be able to add an extra control variable to the usual electronics, known as spin. In this context, the spin represents an intrinsic magnetic moment of the electron, which in principle has random values. In spintronic materials, the orientation of the spin, which was previously thought to be completely random, is now controllable for short times (1 millisecond = 1/1000 seconds). Adding an extra parameter to the information carried by the electron. Taking advantage of the charge and spin property of the electron, these new bits with an extra variable, result in faster electronics, higher capacity, and a step closer to quantum computing.

Seeking to improve the way of understanding the operation of these devices and optimize their performance, in the last decade materials known as dilute magnetic semiconductors (DMSs) have been studied [14–17]. These materials consist of macroscopic systems of low dimensionality that exhibit spintronic properties [17,18]. A DMS consists of an embedded semiconductor matrix, in low proportions (<10%), with atoms of material with magnetic properties [19]. A requirement to obtain a functional DMS is the non-existence of agglomerations or nanostructures of the dopant magnetic material in addition to the non-existence of crystalline phases associated with magnetic ions [20,21].

The development of DMSs based devices was around 8000 papers per year in the last decade, all of these trying to find an optimal configuration of this semiconductors matrix and its dopants to reach a reproducible and functional material to improve the current technology [22]. The biggest problem with DMSs based on the usual semiconductors is their low Curie temperature, which limits them to laboratory scenarios and makes their development as a commercial device impossible [23].

Beginning with magnetic semiconductors whose spin control properties were observed below 100 K [24], semiconductor oxides, revolutionized the researches by exhibiting (computationally by Dietl and Ohno, 2000 [25]) ferromagnetic behavior at room temperature, and experimentally confirmed in different systems [26–32].

The growth of these doped semiconductors is usually at high temperatures by Molecular
Beam Epitaxy (MBE), an expensive synthesis technique that consists basically of putting atom by atom over a perfect oriented substrate in ultra-high vacuum \[33,35\]. The results with this method set the tone in the development of the devices, but the high costs and the speed of production are not a solution for the already named growing market \[36\]. To be able to take a significant step, it is a necessary development in the already revolutionary magnetic seismic oxides, achieving reproducible results, scalable and at a low cost.

Among the semiconductors that have attracted attention to these applications are, among others, the semiconductor oxides based on $TiO_2$, $ZnO$, $SnO_2$, $Cu_2O$, etc. In particular, Zinc oxide ($ZnO$) has been widely studied in different nanostructures, due to its particular electrical, structural, magnetic, chemical, and optical properties. This broadband semiconductor, so-called because of its wide gap, has a stable hexagonal structure, turns out to be friendly to the environment (null toxicity), and has an electronic behavior as a semiconductor. The incorporation of atoms in said matrix, known as doping, usually results by substitution of magnetic ions ($Mn$, $Co$, $Fe$, etc.) or by vacancies of oxygen. The doping results in a structure with a magnetic moment different from zero, allowing the exploitation of the magnetic properties of the material.

Current research in DMSs based on ZnO is centralized on expensive synthesis techniques on perfect crystals as substrates, such as Molecular Beam Epitaxy deposit on sapphire or zirconium substrates. Other techniques involve toxic or dangerous reagents and do not produce a homogenous thin film, which limits their reproducibility and scalability. The sputtering method is an intermediate solution, between characteristics like high costs and low homogeneity. This synthesis technique consists of extracting atoms of a high purity target by an attack with ions of a plasma. The extracted atoms travel to the substrate, where diffusion processes determine the growth of the thin film.

To solve how to prepare optimal DMSs based on oxides magnetic semiconductors using a lower-cost synthesis technique and what are the best synthesis parameters for spintronic applications, this proposal is based on the use the sputtering as a synthesis technique, that is already implemented in several industries, low cost compared with MBE, an atom-by-atom deposit technique (which helps to avoid the formation of clusters or secondary phases) and optimized in the research group in which the project was developed. The growth by sputtering is thin film and can be carried out on any surface. To avoid the problem of degradation with the environment and take advantage of theoretical and experimental background on a material well developed in other areas, $ZnO$ was used as a semiconductor matrix in the project scope and looking for an optimal response as spintronic atoms of Co as dopants. The best synthesis parameters in DC-Magnetron co-sputtering of doped $ZnO$ thin films for spintronic applications were determined and, finally establishing a guide for future investigations in this material for its application as a spintronic device.
This work reports the synthesis, characterization, and modeling of the Co-doped ZnO and its correlation with the synthesis parameters by DC-magnetron co-sputtering. After synthesizing thin films, these were characterized as a function of the synthesis parameters: deposition time, target power, annealing processes, among others. ZnO : Co thin films with different concentrations of Co were fabricated using the optimal synthesis parameters and by a study of the electrical properties were improved its applicability in spintronic systems.
2. **Co-doped ZnO as Oxide Diluted Magnetic Semiconductor**

In this chapter, generalities of Cobalt doped ZnO are approached, doing a state of the art compendium that summarizes the last researches in ZnO as an Oxide-diluted magnetic semiconductor, that will be thoroughly deepened in the next chapters as being necessary. Also, a theoretical and experimental review is presented, finishing with the synthesis description and parameters that were used in the fabrication of the Co-doped ZnO samples.

### 2.1. State of the art: Generalities

The semiconductor oxides are a family of materials whose advantage is not found in their mechanical properties but their electrical, structural, magnetic, chemical, and optical characteristics [37]. The applications of these semiconductor matrices are based on two characteristics: the presence of cations with different valence states and an adjustable oxygen deficiency due to oxygen vacancies [38]. Physical properties are adjusted by altering or varying any of these characteristics, generating possible technological exploitation of these materials. Among the most important applications of semiconductor oxides are their use as gas sensors [39] and the manufacture of transparent conductive electrodes in solar cells [40], flat screens, organic LEDs [41] and other electronic devices [42].

At the nanostructured level, these oxides may manifest some of their altered physical properties, modified or even appear new properties concerning those of the material with a larger scale constitution. The essential components of transparent electronic devices are broadband semiconductors, where the different oxides participate actively, even replacing traditional semiconductors such as silicon [43], gaining special attention during the last years and establishing itself today as one of the most promising technologies to lead the next generation of screens due to its excellent electronic performance [44].

Semiconductor oxides, especially amorphous ones, can be produced at relatively low temperatures (< 500°C) and still have highly homogeneous surfaces, whose electronic performances do not depend on the degree of order of the films [45]. These materials represent a revolutionary idea and exhibit interesting properties, such as high optical transparency, high electron mobility, and amorphous micro-structure [46]. Also, these do not have grain limits,
so the main limitation of mobility in poly-crystalline semiconductors is avoided, which is a great advantage for the integration of electronic processes [47].

Among these semiconductors, Zinc oxide is a very promising material for its application as a semiconductor [36, 48–51]. It has a wide bandwidth of direct transition in the spectral region close to UV radiation [52–56], and high binding exciton energy [52–55][53–56]. The processes of excitonic emission in this material can be maintained at high temperatures, equal to or more than room temperature [54, 57]. ZnO crystallizes in the structure of wurtzite, the same as GaN, but, on the contrary, ZnO is available as large crystals [54].

ZnO properties have been studied since the early days of semiconductor electronics [58], but the use of ZnO as an emergency semiconductor in electronic devices has been hampered by the lack of control over its electrical conductivity. ZnO crystals are almost always of type n, whose cause has been the object of extensive debate and investigation [52–56]. With the recent success of nitrides in optoelectronics, ZnO has been considered as a substrate for GaN, to which it provides a close coincidence [54]. During the last decade, we have witnessed a significant improvement in the quality of ZnO mono-crystal substrates and epilaxial films [36, 48–51]. This, in turn, has led to a reactivation of the idea of using ZnO as an optoelectronic or electronic material in its own right.

The possibility of using ZnO as a complement to GaN in optoelectronics has led many research groups around the world to focus on their semiconductor properties, trying to control the involuntary n-type conductivity and achieve p-type conductivity. Theoretical studies, in particular, the calculations of the first principles based on the functional theory of density (DFT), have also contributed to a deeper understanding of the native point defects and impurities on the conductivity in the ZnO [59–65]. However, acceptance of doping has remained challenging, and the key factors that would lead to reproducible and stable p-type doping have to be yet identified [36, 48–51]. The transition metals have been introduced to the semiconductor matrix, retaining the electrical properties of the material as semiconductor, but also add new and interesting properties to the material.

Diluted Magnetic Semiconductor materials (DMS) are semiconductors doped with magnetic impurities, where doping atoms are replaced more or less randomly at the host crystal sites where they introduce local magnetic moments. These have attracted interest in the past years due to the combination of semiconductor and magnetic properties within the same material [66, 67]. One of the potential applications that DMS materials can offer is to exploit both the charge and the spin of the electron. Physical properties, such as bandgap or magnetism, now turn out to be functions of particle size and, besides, the level of doping. Therefore, ordered arrays of Nano-sized magnetic semiconductors are promising components for new devices in magneto-electronics or spintronics.
However, the low Curie temperature and the low reproducibility of these magnetic semiconductors have limited their application. These seemed to be one of those research topics whose glory belonged to the past. Fortunately, at the beginning of the nineties, \cite{68-70} the ferromagnetic order was discovered in the DMS III-V with critical temperatures that reached 170 K, which has renewed and intensified the interest in these materials. The semiconductor version of spintronics has also attracted researchers because of the hope of participating in efforts to build quantum information processing devices. While these hopes and expectations have not yet been met, the effort continues, as a good example of recent achievements, quantum dots that contain a single magnetic ion result in a huge advance in experimental quantum information \cite{71}.

The nanostructured metal oxides have received a lot of attention and have produced different results with respect to the existence of room-temperature ferromagnetism (RTFM), which has been observed in both pure and doped oxides, in nanoparticles of \(SnO_2\), \(CeO_2\), \(ZnO\), \(TiO_2\), among others \cite{21, 31, 72-75}. The variations reported in the results and conclusions are quite controversial; however, it appears that the observed magnetism is affected by particle size, grain boundary area, defects, surface coating, and/or doping \cite{32, 76-78}. Experimental research on doped oxide semiconductors with Transition Metals (TM) has attracted a lot of interest after the prediction that \(ZnO\) is a promising type for a DMS, due to its predicted RTFM \cite{79}.

\(ZnO\) thin films are generally n-type due to the electronic doping defects originated in Zn interstitial, O vacancies in the \(ZnO\) network, or impurities including hydrogen. Recently, Bououdina et al. \cite{80} studied electron properties polarized by spin and discovered that oxygen plays an important role in the magnetic properties observed in \(ZnO\) systems doped with \(Fe\), \(Ni\), \(Mn\), and \(Co\). In general, experimental studies are carried out at high temperature by expensive techniques, such as deposition by molecular beam epitaxy or ion implantation, so a study with a more industrialized, less expensive technique that allows the deposit at low temperatures is an important step for the science of the DMS itself.

2.2. Experimental aspects

As DMS matrix, \(ZnO\) has studied since Dietl et. al. \cite{25} predicted that Curie Temperature can increase above room temperature, especially in wide-band-gap semiconductors. After the first report of \(ZnO\) as DMS with \(Mn\) doping \cite{81}, many studies on \(ZnO\) doped have been reported with several TMs. However, there is no agreement in the existence and explanation of ferromagnetism. A few studies claim non-ferromagnetic behavior of \(ZnO\)
2.2 Experimental aspects

doped with TM \[81–85\], whereas other research claim ferromagnetic behavior of the same compounds \[86–94\]. The reported values of \(T_C\) scatter from 30 to 550 K and there are strongly correlated with the synthesis conditions. Also, most studies \[95\] report a hysteresis loop in magnetization-field measurements in Cobalt doped \(ZnO\) and that is their principal argument to claim ferromagnetism behavior. Fabrication of \(Co\)-doped \(ZnO\) thin films has been performed by several synthesis techniques. The surface morphology and bulk structure have a strong dependence of the preparation process \[90\]. Authors have reported successful synthesis of \(Co\) doped \(ZnO\) nanostructures by Cobalt implanted \[96\], pulsed laser deposition \[97,98\], chemical vapor deposition \[99\], sputtering \[100\], solid-state reaction technique \[101\], ultrasonic spray technique \[102\], spin-coating \[103\], spray pyrolysis \[104\], sol-gel method \[105\] and molecular-beam epitaxy \[106\].

The deposit by sputtering is a technique of physical vapor deposition that takes advantage of the collisions of an ionized gas (plasma) on a material, commonly known as the target, to release atoms, clusters, or molecules from this through energy transfer of the collisions, to form a thin film on the surface of a substrate. The deposition by this method with two simultaneous targets is known as co-Sputtering, which allows controlling the stoichiometry of the deposited film. The sputtering technique has certain advantages over other forms of synthesis: the uniformity of the films, the thickness control \[107\], the deposit at low temperatures, the variety of materials that can be sputtered, the possibility of synthesizing mixtures and alloys, the good adhesion of the deposited film and the deposit rate control \[108\]. The basic sputtering process has been known for many years and a variety of materials have been successfully deposited by this technique \[109\]. However, the process is limited by low deposit rates, low plasma ionization efficiencies, and a large substrate heating effect. These limitations have been overcome by the development of Sputtering with balanced magnetrons and, more recently, by Sputtering with unbalanced magnetrons \[110\].

From its origins in 1852, where Sir William Robert Grove described the phenomenon, to more recent research has improved the physical understanding of the Sputtering technique resulting in various industrial applications such as lens coatings \[111\], microelectronic devices \[112\], solid-state transistors \[113,114\], among others. The depositing process is carried out in an airtight chamber that, to have the necessary connections to achieve vacuum conditions, also has two surfaces in opposite positions, where target and substrate are held; there are models with several targets to make a simultaneous or multi-layer synthesis. The system must have the necessary gas inlets and connections that allow controlling the synthesis parameters into the chamber. Depending on the reactive nature of the gas, two types of sputtering are distinguished: reactive and non-reactive. In the first one, the ionized gas \((O_2, N_2,\ldots)\) reacts with the target, forming compounds \((TiO_2, TiN\ldots)\) and the non-reactive sputtering is where the gas is inert; usually \(Ar\) is used, due to its low ionization energy \((1520, 6 \text{ kJ / mol})\), its high molecular mass \((39, 948 \text{ u})\) and its moderate cost \[115\]. Accord-
ing to the nature of the voltage used to ionize the gas, the Direct Current (DC) and Radio Frequency (RF) sputtering are distinguished, where RF uses alternating current at radio wave frequencies to avoid charge build-ups on conductive targets [116].

If the ionized gas is directed from the substrate to the target by an electric field, it is said to be Diode type Sputtering. On the contrary, in the magnetron sputtering the gas ions are carried towards the target by a magnetic field, this magnetic field is produced by a magnetron (high current cooled coil) that directs the ions in the gas, increasing their linear momentum and confining the plasma to the surroundings of the target. The magnetron is said to be unbalanced when the field lines reach the substrate and allow the attack of the gas ions on the surface of the substrate and balanced when the field is restricted to the target. Furthermore, the magnetron is said to be compensated when the generated magnetic field takes into account the magnetic nature of the target and compensates for the magnetization caused in response to the imposed field.

### 2.3. Synthesis characteristics

Samples were synthesized by DC magnetron co-sputtering, in a high-vacuum chamber. ZnO and Co targets of 76, 2 mm diameter, 3 mm thick and 99.9% purity (see Appendix A), were used with a 70 mm substrate-target distance. Unlike ceramic ZnO target, Cobalt target was sputtered in a compensated magnetron, due to its magnetic response. Both targets inclined 10° to the substrate perpendicular line.

Before thin-film synthesis, the chamber was cleaned with acetone, isopropanol, and dried with N₂; also, after each deposit chamber was cleaned with isopropanol and dried with N₂. Before reaching optimal conditions in the sputtering system, high-vacuum conditions were achieved (\( \sim 8 \times 10^{-4} \) Pa), then a high purity N₂ (99,999%) flux was introduced to the system, as drag gas (\( f_{N_2} = 20 \) sccm by 3 minutes). Finally, high vacuum conditions were sustained while temperature conditions were reached in the substrates. Once the temperature was stabilized (±3°C), a high purity Argon flux (99,999% at \( f_{Ar} = 20 \) sccm) was constantly injected into the system and a pressure valve was used to fix the chamber pressure work (\( P_w \)) in 3,3(1) Pa.

All thin films were synthesized in the same \( P_w \) on different substrates: soda-lime glass, Alumina (\( Al_2O_3/Glass \)), Indium Tin Oxide (ITO/Glass), Gold (Au/Glass), Titanium (Ti sheet) and Silicon (Si n-type). All Glass substrates were cleaned following a standardized process: Soap bath, Alconox [117] bath in ultrasound by 15 minutes, distilled water washed, acetic acid (\( CH_3COOH \)) bath, hydrogen peroxide (\( H_2O_2 \)) bath, deionized water bath in ultrasound by 15 minutes, isopropanol washed and N₂ drying.
2.3 Synthesis characteristics

Al and Au films over glass were deposited by thermal evaporation; ITO, Si, and Ti substrates were bought with laboratory standards (see Appendix B). Al₂O₃ substrates were synthesized by thermal-dry evaporation. The Si was oxidized by a natural process. Both oxidation processes were performed at 74, 6 kPa and high relative humidity. All substrates were stored in a dehumidified vacuum chamber and, just before starting the synthesis, blown with high purity N₂. Fig. 2-1 shows a schematic diagram of the sputtering chamber and the substrates distribution.

Substrates had always the same distribution inside the chamber, and due to the distribution of the targets, thin films width and Co concentration have a strong dependence on that position. For this reason, the position of the substrates were fixed for all synthesis.

One of the most important conditions to achieve a novel, functional and precursor spintronic material is the existence of intrinsic magnetic properties without magnetic crystal phases. The probability to have secondary phases in the semiconductor matrix is highly dependent on the synthesis method and cobalt concentration. The substrates that are closer to Co target have more Co concentration than others; to increase the concentration of Cobalt
in each substrate position, sputtering power was varied in a range of 20 W to 60 W to the Cobalt target, and keep fixed in 100 W on the ZnO target.

Due to the ceramic nature of the ZnO target (Low thermal conductivity), reach a DC power of 100 W is not easy (295, 7(1) V at 0, 338(1) A). Target manufacturer recommends 20 W/sq^2 for the maximum power and 20 W/min of maximum power increase \(^{[118]}\), for this reason, a power gradual increment was done until 100 W. When this power was reached, the Co magnetron was turned-on directly in the required power and one minute of co-sputtering was done to clean the target surface, then shutters were opened for the corresponding deposit time.

First to all, a couple of series were performed without Co impurities to study the growth of the semiconductor matrix. In these series, the ZnO target power (80 W, 100 W, and 120 W) was varied. After some structural and composition analysis, the 100 W target power was established as the optimal-safely. Different deposit times, temperatures and Co-target power were used to achieve an optimal ZnO-based DMS. Table 2-1 shows the different variable parameters. The other deposit parameters were remain constant: work pressure \((P_W = 3, 3(1) \text{ Pa})\), Argon flux \((f_{Ar} = 20, 0(1) \text{ sccm})\) and, ZnO-target power \((P_{ZnO} = 100, 00(5) \text{ W})\).

### Table 2-1.: Different synthesis parameters for the ZnO and Co-doped ZnO thin films series.

<table>
<thead>
<tr>
<th>Series (Label)</th>
<th>Substrate Temperature (T_s ) (^{\circ} \text{C})</th>
<th>Sputtering time (t_d) (min)</th>
<th>Co-target power (P_{Co}) (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>150(2)</td>
<td>15,00(1)</td>
<td>0</td>
</tr>
<tr>
<td>A2</td>
<td>20(4)</td>
<td>15,00(1)</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>150(2)</td>
<td>15,00(1)</td>
<td>20,00(5)</td>
</tr>
<tr>
<td>C</td>
<td>150(2)</td>
<td>15,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>D</td>
<td>150(2)</td>
<td>15,00(1)</td>
<td>60,00(5)</td>
</tr>
<tr>
<td>E</td>
<td>150(2)</td>
<td>15,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>F</td>
<td>150(2)</td>
<td>15,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>G</td>
<td>150(2)</td>
<td>20,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>H</td>
<td>150(2)</td>
<td>30,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>L</td>
<td>20(4)</td>
<td>15,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>M</td>
<td>50(3)</td>
<td>15,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>N</td>
<td>100(3)</td>
<td>15,00(1)</td>
<td>40,00(5)</td>
</tr>
<tr>
<td>O</td>
<td>150(2)</td>
<td>15,00(1)</td>
<td>40,00(5)</td>
</tr>
</tbody>
</table>

We need to find an optimal configuration to have a tetrahedral position of Co in the ZnO
matrix. As is well known, diffusion and species mobility constants are higher when the temperatures rise. For this reason, higher temperature exposure was the best option to give the system the necessary energy to reach the stablest configuration. Once finished the deposit, was studied the effect of an \textit{in situ} annealing on two samples (one fabricated at room temperature $\sim 300$ K - and another at 423 K). We analyzed the magnetic properties to determine if the annealing thermal energy was necessary to have optimal conditions to achieve a ZnO based DMS. Possible Co magnetic contributions were observed in a competition with the ZnO diamagnetic nature only when the samples were annealed. For this reason, all samples were annealed \textit{in situ} by two hours at 473 K.
3. $Zn_{1-x}O_yCo_x$ Density Functional Theory approach

Among the II-VI semiconductors, the $ZnO$ is a material with wide bandgap energy ($E_g = 3.35$ eV) that has a transparent characteristic in the visible, then once doped with transition metals would be an interesting ferromagnetic material. Wurtzite is the most stable $ZnO$ crystalline structure (hexagonal, with $a = 3.25$ Å and $c = 5.12$ Å) [119]. This oxide has naturally an electron conductivity ($n$-type) but with certain doping types, $p$-type conductivity can be induced [29]. Besides, the possibility of inducing room-temperature (RT) ferromagnetism (FM) in Diluted Magnetic Semiconductors (DMS) based on $ZnO$ have attracted plenty of interest [25, 120–122]. Since Dietl predicted a Curie temperature ($T_C$) above room temperature in $Mn$-doped $ZnO$, DMSs based on this semiconductor had raised great interest [25], being emerged as a leading candidate for spintronic due to its special semiconductor characteristics and spin properties.

Cobalt doped $ZnO$ has become a focus of attention as one of the possible doping types due to its high Curie temperature reported, even of up to room temperature (RT) and a controllable FM ordering [123, 124]. Coupled with $ZnO$ current and well-studied electrical and optical characteristics, the addition of a controllable magnetism will make it a technologically novel and attractive material. Previous reports have shown that at Co concentrations of less than 10% there is a substitution between Cobalt and Zinc atoms, with a +2 charge state [125]. $Co(II)$ (with $3d^74s^0$ configuration) as Zn-substitutional in the wurtzite structure results stable and occupies a fourfold tetrahedral coordination site, causing that the $t_d$ crystal field splits the $Co - 3d$ states into lower $e_d$ and upper $t_{2d}$ states (typically on the order of $1.5 - 2.0$ eV), resulting in a spin-oriented occupation with a local $Co$ magnetic moment close to $3\mu_B$. [126].

However, experimental reports on $ZnO$-based DMS have been highly conflicting in reproduce these predictions. It was found to be paramagnetic [86, 127, 128], and in some situations were reported ferromagnetism in some samples [90, 120], with a strong dependence on methods and conditions of synthesis [129, 130]. Magnetic ordering seems to be susceptible to the chemical ordering of the $Co$ dopant and other impurities such as interstitials and vacancies in the lattice. Spintronic applications [82] usually require that ferromagnetism has an intrinsic origin, i.e., not from magnetic Cobalt clusters or impurity phases [131].
3.1 State of the art: Computational approaches

One way to study the Co-doped FM materials is based on the 3d band coupling \[132\]. How ZnO is a wide gap semiconductor, minority spin Co \(t_{2g}\) states would place within the bandgap, reported from ZnO:Co optical and magnetic measurements ZnO:Co \[125,133,134\]. Surprisingly, once again some previous theoretical and experimental studies are not in agreement \[23,135,136\]. It has been made clear that different reports disagree, even among similar models and techniques. It is not clear what is the best setup in Co-doped ZnO or the most accurate model to explain the magnetic interactions.

In this chapter, we studied the role of oxygen vacancy (\(V_O\)) near cobalt impurities in the ZnO matrix, trying to achieve an optimal configuration for the room temperature ferromagnetism that have been reported by experimental studies \[90,120,129,130\]. Different configurations were performed, varying the positions and concentrations of Co and \(V_O\). The stability of these systems was determined by the formation energy calculations. To understand the magnetic ordering, the DOS and spin-charge spatial distributions were compared between the most stable configurations. The idea to have interplaying charge and spin degrees of freedom accommodated into a semiconductor material at room temperature is expected to explore novel physics and new devices, such as spin valves.

### 3.1. State of the art: Computational approaches

Several computational methods based on density functional theory have been extensively used for study the electrical, structural, optical, and magnetic properties of ZnO \[137\]. It is well known that DFT conventional methods produce underestimated value of the energy bandgap (\(\sim 0.7 - 1.0\) eV) compared with the experimental value (\(\sim 3.4\) eV). The error has been discussed in the literature, for this and other larger electronic \(d\) and \(f\) orbital systems \[138,139\]. In the last two decades, several approximations, have been proposed for a better result on the electronic localization of those electrons. Besides, these corrected approaches have also been successfully used in the calculation of defects, surfaces, and interface properties \[140,141\]. Although this error, the spin-charge distribution is well estimated under conventional DFT methods and it is been frequently discussed in most published articles \[137,142,144\]. GGA+U, as bandgap correction method \[145\], introduces an effective Hubbard \(U\) to count for the \(d\) electrons of transition metals to improve the estimation of the bandgap. The corrected bandgap as a function of the Hubbard \(U\) has been shown that various \(U\) values give a consistent improvement of band gap for different phases of ZnO, for GGA \[146\]. Since GGA calculation is less computationally expensive than GGA+U, if we are not interested in band-gap calculations, GGA is enough to have a first approach to the structure and magneto-electric properties.

Several theoretical studies based on ab initio methods have focused on the study of hexag-
ZnO. Even though there are a lot of studies about its other crystal structures, including rocksalt, CsCl structure type, zinc-blend, and wurtzite have been reported [147, 148]. The thermodynamically stable phase of ZnO at ambient condition is the hexagonal structure (Wurtzite) which is fourfold-coordinated. The zinc-Blend structure is another similar structure that can be stabilized by the epitaxial growth of ZnO on cubic substrates. The properties of each lattice are well studied, theoretically and experimentally. For the wurtzite cell, the theoretical $a_0(c_0)$ constant takes values around 3.1Å−3.3Å(5, 10Å−5, 30Å) [146, 149, 150], while the experimental value in pure-wurtzite systems has been reported as 3.25Å(5, 204Å) [145].

### 3.2. Theoretical aspects

The foundation of the first-principles method is based on quantum mechanics description of the behavior of electrons and atomic nuclei [151]. The Schrödinger equation serves as the basic equation here, where the Hamiltonian operator consists of kinetic and potential energies due to the Coulomb interaction between electrons and nuclei:

$$\hat{H} = \sum_{l=1}^{N} \frac{P_l^2}{2M_l} + \sum_{i=1}^{n} \frac{P_i^2}{2m_i} + \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} + \sum_{l \neq j} \frac{Z_l Z_j e^2}{|R_l - R_j|} - \sum_{ij} \frac{Z_l e^2}{|R_l - r_i|},$$  \hspace{1cm} (3-1)

where $P_l$ ($p_i$) are the momenta of ions (electrons), $R$ ($r$) represent the coordinates of ion (electron), $Z$ ($e$) is the charge of the ion (electron), and $M$ ($m$) are their masses. Due to the complexity of the Schrödinger equation, it is almost impossible to be solved and would lead to uncontrollable computation in a system of multiple electrons. This is principally due to their interaction nature which each other, which leads to many-body problem [151, 152]. Several approximations are then developed to solve this. The first useful one is the well-studied Born–Oppenheimer approximation [153, 154]. The principal idea in that approximation is to separate the electron and nuclear motion [152]. This is because the mass of the nucleus is much larger than the electron’s, and the nuclei are principally fixed particles. Uncoupling that, eventually enables the possible application of the Schrödinger equation in a complex system.

Hohenberg and Kohn (1964) [155] developed a couple of theorems that defined the electron density as a unique function for ground state energy of a system with $N$-electrons. Hohenberg-Kohn theorems have served as the basis for modern DFT. The first theorem stated that in a system with $n$ interacting electrons, the many-body ground state wavefunction ($\Psi_{(r_1,\ldots,r_n)}$) of all electrons is a unique functional of the electronic density, $\rho(r)$ [155]:

$$\rho(r) = n \int \cdots \int |\Psi(r_1,\ldots, r_n)|^2 \, dr_1 \cdots dr_n. \hspace{1cm} (3-2)$$
As the Hamiltonian equation comprised of the sum of several terms (electronic kinetic energy $T$, the attraction of electron-nuclear $V_{Ne}$, and electron-electron repulsion $V_{ee}$), the molecular property based on these average variables is determined by ground-state electronic wave-function $\rho_0(r)$. So, the total energy can be calculated as the sum of average quantities.

Now, considering $v(r)$ as a function for nuclear potential energy for an electron at point $r$, the energy of the ground state is:

$$E_0 = E_v[\rho_0] = \bar{T}[\rho_0] + \bar{V}_{ee}[\rho_0] + \int \rho_0 v(r) dr; \quad (3-3)$$

the first theorem focuses on the wave-functions and energy functionals. The second one allocates a minimum principle for density. It stated that the ground state energy of any trial electron density cannot be smaller than the true ground state system:

$$E_v[\rho_{tr}] = E_v \geq E_0 = E_0[\rho_0]. \quad (3-4)$$

After those theorems, a Schrödinger-like equation with a modified effective potential had been introduced, by adding a set of the independent-particle equation much easier to solve (Kohn and Sham [156]). This fictitious supporting system is used to resemble the true many-electron system, and write the energy as a numerical solvable set:

$$E_v[\rho] = \int \rho(r)v(r)dr + \bar{T}_{s}[\rho] + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 + E_{XC}[\rho]. \quad (3-5)$$

$E_{XC}$ is known as the exchange-correlation energy that contains the correlation energy, exchange energy, Coulomb correlation energy, and self-interaction correction. No exact expression for this exchange and correlation ($XC$) potential is known [157]. So, to ensure the accuracy of DFT calculation an approximation is thus embodied. There are a lot of approximations that have been developed (LDA, GGA, meta-GGA, and hybrid functional).

Each of these conveys different definitions and approaches. Usually, the LDA and GGA are the ones widely used in the DFT calculation of the ZnO system [144,158,159].

The idea of LDA is: for a given region of material with a slow varying in charge density, the $XC$ energy at point $r$ is only dependent on the particle density at that point, $n(r)$ [160]. This $XC$ energy must be similar to homogeneous electron gas ($e^{hom}$) of the same charge density:

$$E_{X_C}^{LDA} [n(r)] = \int n(r)e^{hom}_{XC} [n(r)] dr \quad (3-6)$$

Even with the new advances in material science, it has been successfully calculated the properties of different materials with predictive accuracy [157]. However, the localized characteristic in LDA has enabled the incorrect treatment of the electronic structure of certain materials, especially in a system with a strongly correlated structure [158,161,162]. ZnO is an example of a strongly correlated structure owing to the full electrons at Zn – 3$d$ state.
For this reason, generalized gradient approximation is more used in this system. This second approximation uses two variables instead of one, the electron density and its gradient:

\[ E_{XC}^{GGA} = \int n(r) e_{XC}^{\text{hom}} [n(r), \nabla n(r)] dr, \]

also, some corrected functional functions have been developed in GGA formalism to include the contribution of exchange and correlation part \[163,164\].

### 3.3. Methods and model

The spin density functional theory (DFT) was used with the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof (PBE) for exchange-correlation functionals \[163\], as implemented in the VASP package \[165,166\]. The electron wave functions were described using the projector augmented wave (PAW) method of Blöchl in the implementation of Kresse and Joubert \[167\]. For DFT calculations, two periodic orthogonal super-cells, with 16(8) and 36(18) formula units (single-cells) of ZnO were used, containing 32 (16) or 72 (36) atoms (Molecules), which have lattice vectors \((0; \sqrt{3}a/2; 0), (3a/2; 0; 0), (0; 0; c)\) (see Fig. 3-1).

![Figure 3-1.](image)

Figure 3-1.: Wurtzite single cell, with two different tetrahedrons, of Co-doped (Blue spheres) ZnO (left) and 332 super-cell (F-Configuration in Table 3-1). Large yellow (small whitish) spheres designate Zn (O) atoms.

In all the different configurations performed (see Table 3-1), plane waves have been included up to cutoff energy of 520 eV, energy difference for ionic convergence was set to 1 meV and
electronic states were occupied with a Methfessel-Paxton smearing width of 0.20 eV in a real-space projection scheme, used for efficient computations.

<table>
<thead>
<tr>
<th>super-cell</th>
<th>Single Cells (#)</th>
<th>Impurities</th>
<th>Co – Co Distance Å</th>
<th>Conf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>222</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 6.25% 0 0.00% 6.58(1)</td>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 6.25% 1 6.25% 6.58(1)</td>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1 6.25% 2 12.50% 6.58(1)</td>
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Table 3-1.: $\text{Zn}_{1-x}\text{O}_x\text{Co}_x$ systems studied (A-H configurations) at different $V_O$ and Co composition, in 222 or 332 super-cells and its Co – Co characteristic distances.

To calculate the formation energy of each Co-doped and O-vacancy configuration. First, we carried out total energy calculations for Co-atom, Co-bulk, Zn-atom, Zn-bulk, $O_2$ molecule, and $ZnO$-wurtzite, and then we calculated these energies for the Co-doped $ZnO$ system. Formation Energy ($E_f$) and Cohesive Energy ($E_c$) were calculated as [168]:

$$E_{c,(f)} = \mu_{ZnO} - \mu_{Zn(2)} - \mu_{O(2)},$$

(3-8)

where $\mu_{ZnO}$ is the total energy per atom pair of $ZnO$ compound, $\mu_{Zn}$ is the isolated atom energy of $Zn$ for $E_c$ (energy per atom of bulk $Zn$ for $E_f$) and $\mu_{O}$ corresponds to isolated atom energy of $O$ for $E_c$ (energy per $O$ atom in the $O_2$ dimer for $E_f$). Co-doping and the formation energy calculations for impurities were performed using [168]:

$$E_F = E_{\text{tot}} - \left( E_{\text{tot}} [\text{host}] + \sum \eta_i \mu_i \right),$$

(3-9)

where $E_{\text{tot}}$ is the total energy for the super-cell with impurities, $E_{\text{tot}} [\text{host}]$ is the total energy of the host super-cell, $\eta_i$ indicates the number of atoms type $i$ that are added ($\eta_i > 0$) or substracted ($\eta_i < 0$), and $\mu_i$ is the chemical potential of the $i$ species.

With the same computational parameters, previous calculations were performed with different kinds of impurities in the $ZnO$ matrix (Oxygen vacancies, Zinc vacancies, $Co_O$ substitution, $Zn_O$ anti-site, and $Co_Zn$ substitution). Also, combinations of these impurities
at different concentrations were studied. Figure 3-2 shows the formation energy of these configurations ordered from the lowest to the highest. Based on this, we can predict that is more probable to have one or another kind of impurity, at determining the energy. After that, the configurations were restricted to the Cobalt-Zn substitution and Oxygen Vacancies.

The absolute errors were calculated based on statistical dispersion of the data and error propagation, the number in parenthesis is the one-sigma (1σ) uncertainty in the last two digits of the given value. The previous calculations and the corresponding values to undoped super-cell were according to previous reports. Our results $E_c = -7.01(2)$ eV and $E_F = -2.95(1)$ eV are in good agreement with theoretical ($E_c = -7.69$ eV and $E_f = -2.89$ eV) [169, 171] and experimental ($E_c = -7.52$ eV and $E_f = -3.56$ eV) [172] results reported by other authors. However, we can observe that the GGA approach tends to underestimate the formation energy values. After determining the energies associated with undoped systems, it is necessary to determine, under our model and approximations, the most stable configuration for each type of doping, Co impurities and oxygen defects (Interstitial Cobalt, Zn and oxygen vacancies, Co-Oxygen and Zn – O antisites, and Co – Zn substitution at 2.78%, 5.56% and 6.25% with and without Oxygen vacancies). Once determined the

![Figure 3-2: Formation Energy for different impurities configurations in the ZnO matrix.](image)
3.4 Results and discussion

stability range of Oxygen vacancy doped in $\text{Zn}_{1-x}\text{O}_y\text{Co}_x$ systems, we perform a series of simulations varying the shortest distance between Cobalt and $V_O$, at different $Co$ concentrations (Table 3-1 B, D, E, and H configurations). In the most stable $Co - V_O$ system was added a second $V_O$ at different positions (Table 3-1 C and F configurations). After VASP simulations, using the VESTA software we analyzed the spin density distribution in different planes to show how the oxygen vacancies affect the magnetic distribution inside the structure. Spin density plots were analyzed in the range of $4e^-/\text{Å}^3$.

3.4. Results and discussion

Our structural optimization calculations for $Co$-doped $ZnO$ at a Cobalt concentration of 6, 25% and 3, 12% in $Zn$-substitutional positions, and a $V_O$ concentration of 0%, 3, 12% and 6, 25%, reveal that the distance and the associate substitutional local symmetries have an important role in the structure stability. To study the effect of the oxygen vacancy ($V_O$) on the structural, magnetic, and electric properties of $Co$-doped $ZnO$, in the eight configurations, different positions of oxygen vacancy were adopted. In Fig. 3-1 (right) the different configurations to oxygen vacancies in the super-cell were set varying the $Co - V_O$ distance at different $O$ positions. Different $Co - Co$ distance configurations were also studied.

3.4.1. Effect of $Co - V_O$ distance in the $\text{Zn}_{1-x}\text{O}_y\text{Co}_x$ system

We studied the $Co - V_O$ distance ($\Delta_1$) replacing oxygen by vacancy at different positions, with a fixed $Co - Co$ distance: 9, 87(1) Å (2, 78%Co), 6, 58(1) Å (6, 25%Co), and twice $Co - V_O$ distance (5, 56%Co). After calculated the most stable magnetic configuration ($V_{O1}$ around 1, 90(6) Å), we studied the effect of a second $V_O$ at different $Co - V_O$ distances ($\Delta_2$) in 2, 78% Co and 6, 25% Co systems. (Fig. 3-3 (b)). Fig. 3-3 (c) shows the formation energy as a function of $Co - V_O$ distance ($\Delta_1$) for different $Co$ concentrations, the stability of the structure is higher as $\Delta_1$ decrease and all configurations have a magnetic moment in the range of 3, 02(1) $\mu_B/Co$. When the $V_O$ is added, the magnetic moment decrease as $\Delta_1$ (Fig. 3-3 (a)) and is always lower than the calculated without oxygen vacancies (dashed line $\mu_T = 3, 131(1)\mu_B/Co$).

When the second vacancy is added, the effect in short distances (comparable with the first vacancy) differs according to the $Co - Co$ distance. When it is shorter (6, 58(1) Å for 6, 25% Co) the total magnetic moment per cobalt ($TMM/Co$) decreases as $\Delta_2$. In the other hand, for a lower Cobalt concentration (2, 78% Co) and a higher $Co - Co$ distance, $TMM/Co$ increases as $\Delta_2$ decreases. However, when $\Delta_2$ is at least twice $\Delta_1$ in both cases $\mu_T/Co$ trends to the one-near $V_O$ case with $TMM/Co \sim 3, 00(2)\mu_B$, giving us an effective range for the second vacancy. Taking this as a start point, we can analyze the effect of one vacancy near to the cobalt atoms and assume that other far vacancies do not contribute in a significant way.
Figure 3-3.: Effect of $Co - V_O$ distance in (left) the total magnetic moment per Cobalt atom in (a) 1 : 1 ($Co : V_O$) ratio, (b) 1 : 2 ratio and (c) Formation energy, for different cobalt concentrations and one $V_O$ per super-cell.

Different atoms contribute to the $TMM/Co$, as expected, Cobalt mostly, but also, a lower contribution from the semiconductor matrix and the electrons located in the interstitial region. Fig. 3-4 (a) shows the average contributions of these species. The contributions per Cobalt orbital (Fig. 3-4 (b)) is mainly by $d$ orbital (97.67(1)%) where no-compensated electrons are located. The lower contributions of $s$ and $p$ orbitals allow a $d - d$ coupling between adjacent Cobalt or a possible mediated magnetic interaction for electrons trapped in the oxygen vacancies [126].

Figure 3-4.: (a) Average contribution from $Co$, interstitial region, $Zn$ and $O$, to the total magnetic moment per Cobalt atom and (b) contributions per orbital into the Cobalt atom.

In a Heisenberg model, the formation energy difference between ferromagnetic (FM) and
antiferromagnetic (AFM) configuration ($\Delta E_f$) is given by \[173\]:

$$\Delta E_f = (E_{f}^{AFM} - E_{f}^{FM}) = J_0 S(T + 1)$$

Equation (3-10)

and Curie temperature, following \[174\]:

$$k_B T_C = \frac{3}{2} J_0 S(S + 1)$$

Equation (3-11)

We carried out ferromagnetic and antiferromagnetic configurations, at 5, 56% Co and then we add $V_O$ at 2,78%, to study the difference in the formation energy and its respective exchange constant as a function of the $Co - Co$ distance (Fig. 3-5). The stabilization on the magnetic configuration increases as $\Delta E_f$, a positive(negative) value indicates that FM(AFM) configuration is preferred by the structure. When Oxygen vacancies are not in the structure, the energy difference is the smallest, and the most stable structure corresponds to an antiferromagnetic configuration. In almost all the cases, it is shown that the $V_O$ stabilizes the ferromagnetic configuration, reaching a maximum $T_C = 374,88(5)$ K where the two cobalt atoms are closer. The addition of $V_O$ is a mediator in the high-temperature ferromagnetism but its effect on the electronic distribution around the Cobalt atoms remains a question.

Figure 3-5.: Difference between Ferromagnetic ($E_{\uparrow\uparrow}$) and Anti-ferromagnetic ($E_{\uparrow\downarrow}$) formation energies as function of the $Co - Co$ (5,56% Co) distance for configurations with and without $V_O$, the right axis shows the exchange constant $J_0$ in the model Eq. 3-10
3.4.2. Effect of the $V_O$ on the magnetic and electronic properties of Co-doped Zinc oxide

Also, we have studied the electron spin-density (up and down) in Co-doped ZnO with and without oxygen vacancies for the most stable energetical configurations. First, we observe the spin distribution in different crystallographic planes for the case of oxygen vacancy near the Cobalt impurity. We focused on the planes that contain the oxygen vacancy, Cobalt, and other Oxygen atoms near the Cobalt atom. Fig. 3-6 shows the plane ($\bar{1}2\bar{1}0$) section of two comparative scenarios: The right shows a Cobalt atom (blue sphere) in a tetrahedral Zn position with four oxygen (two red spheres in the plane) and the left shows the same configuration but with an oxygen vacancy in this plane; Zn atoms are represented by a silver sphere.

![Figure 3-6](image)

Figure 3-6.: Spin density difference ($\rho_\uparrow - \rho_\downarrow$) section (plane ($\bar{1}2\bar{1}0$)) of Cobalt doped ZnO with $V_O$ (left) and without $V_O$ (right).

The right side of Fig. 3-6 shows a slightly higher $\rho_\downarrow$ in the middle of two oxygen atoms, those zones are present always between any couple of oxygen atoms. Also, on the left side, it is possible to observe a bigger compensated electrons zone (blue-red zone), which explains the lower total magnetic moment when $V_O$ is added. In the $V_O$ site there are $\rho_\downarrow$ and $\rho_\uparrow$ contributions, giving a full-compensated (equal $\rho_\downarrow$ and $\rho_\uparrow$ contributions) spin-density zone. This increment of the antiferromagnetic zones can be explained by the non-coupled electrons from the oxygen removed, that have an exchange interaction ($J_0 < 0$) with the Cobalt electrons.

When the second Oxygen vacancy is added, as we previously discussed, there is a maximum range to affect the total magnetic moment per Cobalt. Figure 3-7 shows a transverse section of the spin density difference in the lower-$\Delta_2$ C-configuration. The plane ($\bar{1}2\bar{1}0$) contains both $V_O$ as the rightest part of the figure shows. In the $\rho_\uparrow - \rho_\downarrow$ plot can be observed
the difference in the spin distribution when the two vacancies are added (left). Contrasting with the one-V\textsubscript{O} part (left part Figure 3-6) there is a new zone of positive spin difference, so the total magnetic moment per Cobalt should increase, as we expected since Figure 3-3 was discussed. Also, the iso-surface (outside-left) shows three negative zones (cyan zones) that have antiferromagnetic interactions with the positive distribution (purple zones) from the Cobalt atom and the electrons of the interstitial region.

Figure 3-7.: Spin density difference ($\rho_\uparrow - \rho_\downarrow$) section (plane ($\overline{1}2\overline{1}0$)) of Cobalt doped ZnO with 12.5\% of V\textsubscript{O} -1\textsubscript{Co} : 2\textsubscript{V}O relation-(left) and without V\textsubscript{O} (right).

We analyzed the antiferromagnetic and ferromagnetic cases when the two Cobalt atoms are closer; Fig. 3-8 shows a cut section (plane (11\overline{2}0)) of these configurations with (left) and without (right) oxygen vacancies. In the ferromagnetic cases, when V\textsubscript{O} is added, we have a lower $\rho_\downarrow$ increment than the previous case, but the $\rho_\uparrow$ zone decreases. This is easier to see in the iso-surfaces representation (Outer), where only the extremes of the scale are showed. This resulted in an average total magnetic moment per Cobalt decreasing (from 2,561(1)$\mu_B$ to 2,481(61)$\mu_B$) due to the V\textsubscript{O}, with proportionality between TMM/Co and Co – Co distance increase.

In the antiferromagnetic case, we have an average total absolute magnetic moment per Cobalt of $|TMM/Co| = 2,55(1)\mu_B/Co$ without Oxygen vacancies and $|TMM/Co| = 2,46(7)\mu_B/Co$ with V\textsubscript{O}. The spin-density-difference zones (Fig. 3-8-(a)) result in a compensated distribution, where is visible an antiferromagnetic interaction inside the shared Oxygen, and between this Oxygen and Cobalt neighbors. Once again, the effect of the V\textsubscript{O} is easier to observe in the iso-surface representation (Fig. 3-8-(a)-outer), where the oxygen zone is wrapped by compensated distributions, but when O is removed, the $\rho_\uparrow$ and $\rho_\downarrow$ spin densities are getting closer to the opposite Cobalt, letting a compensated electrons V\textsubscript{O} zone.

Now, we are particularly interested in the DOS distribution near the Fermi level. DOS provides physical insight into how the interaction of Co impurities and O vacancies on ZnO
26  Zn$_{1-x}$O$_y$Co$_x$ Density Functional Theory approach

occurs, and how these interactions can generate induced magnetism. The total density of state (TDOS) and the partial density of state (PDOS) of the 3$d$−Co, 2$p$−O, and 3$d$−Zn orbitals were calculated in the ferromagnetic most stable configuration with (Figure 3-9-(b)) and without $V_O$ (Figure 3-9-(a)).

Previously we showed that the addition of $V_O$ results in a decrease of the TMM/Co, but with a more stable structure. PDOS statistical analysis showed that the largest PDOS contributions in Co and O are d (87(2)%) and p orbitals (71(1)%), respectively. Based on that, a $p$−$d$ coupling is the best fit model to explain the magnetic behavior of the structure. Comparing the PDOS of Co and O in structures without $V_O$ with the most stable Zn$_{1-x}$O$_y$Co$_x$ structure, we can observe extra spin-down states appear in the O-PDOS (Fig. 3-9-b).

We observed below, on, and above the Fermi level, some impurity energy-level states in the spin-minority region (TDOS in Figure 3-9-(a)) caused mainly by 3$d$−Co states. Compared with the majority spin region where there are no states, it shows a high polarization of spin induced by the Co impurity, indicating that the system is nearly half-metallic. Concerning the PDOS of the 3$d$−Co orbitals, near and below the Fermi level in the minority spin region, this area is divided into four parts, forming peaks of energy bands that indi-

Figure 3-8.: Spin density difference ($\rho_\uparrow - \rho_\downarrow$) section (plane (1120)) and iso-surfaces (outer) of (a) Antiferromagnetic and (b) ferromagnetic configurations. Cobalt doped ZnO with $V_O$ (left) and without $V_O$ (right).
3.4 Results and discussion

Figure 3-9.: Total DOS and PDOS (Co, O and Zn) of most stable structures in Ferromagnetic configuration with 5.56% of Co, (a) without $V_O$ and (b) with $V_O$ at 2.77%. The zero of the energy has been set at the Fermi level, as indicated with dashed lines. The values of the positive (negative) states correspond to the majority (minority) spin regions.

cated localized states. These peaks overlap with four others of lower height, corresponding to the $2p - O$ orbitals. On the other hand, five peaks of unoccupied bands appear above the Fermi level in the minority spin region, caused mainly by states located in an energy range of 0.75 and 1.25 eV. Once again there is an overlap with the other five lower height peaks, corresponding to the $2p - O$ orbitals. All these characteristics present in the PDOS suggest a strong hybridization between the $3d - Co$ and $2p - O$ orbitals, inducing magnetization in the Co atom as well as in the neighboring O atoms, as was observed in the spatial-spin distribution (Fig. 3-6). These results are in agreement with those reported by González-García et al. [175]. In Fig. 3-9(b), compared to the TDOS of Fig. 3-9(a), the states are modified due to the O vacancy. Below and above the Fermi level, in the minority and majority spin regions, extra energy states that emerge in $3d - Co$, $2p - O$ and $3d - Zn$ can
be seen. These states are not exhibited in the PDOS of the $3d - Co$, $2p - O$ and $3d - Zn$ in figure 3-9(a), which suggests that there is a charge transference when the $O$ atom is removed. So, there could be loose bonds in the structure, which are redistributed causing a charge transference toward its first and second neighboring atoms. Due to the presence of $2p - O$ and $3d - Zn$ states near below and above the Fermi level in the majority spin region, the spin-polarization is reduced and the total magnetic moment per cobalt decreasing. We can see this behavior in the previous spin density plots (Fig. 3-6 and Fig. 3-8), where there is a lower increment of $\rho$ when $O$ vacancy is added.

However, in the $3d - Co$ states, the new states introduced in minority spin regions above the Fermi level increasing the local magnetic moment of Co atoms. Below the Fermi level in the minority spin region, the states become more localized and the Fermi level passes through a small part of the impurity states maintains the nearly half-metallic behavior. Given that the $Co - Co$ distance is large enough to ignore the direct coupling between them (see Figure 3-8(outer)), and according to the Bader analysis, there is an appreciable charge transfer between the two Co atoms that could be mediated through $O$ vacancy. The direct exchange interaction $d - d$ between the Co atoms could explain the stabilization of ferromagnetism in this compound. These results are very similar to and consistent with those reported by Walsh et. al. [126]. These results indicate that Co-doped $ZnO$ can be used as a potential diluted magnetic semiconductor in spin-valve devices [176,177].
4. Structural and morphological characterization of Cobalt doped $ZnO$

Spintronic materials are characterized by controlling and having both, electrical and magnetic, properties [18]. To achieve a functional, optimal, and reliable spintronic it is necessary to have control of its structure. $ZnO$ structure has been studied for a long time, and as it was mentioned above, the Wurtzite structure is the most stable. Also, it was checked that the $Co_{Zn}$ substitution is possible and it is not too expensive energetically.

The experimental study of $Co$-doped $ZnO$ thin films starts in this chapter. Here, several properties related to the thin-film structure are studied. First, a brief state of the art is reviewed to have an accurate background of the reported structural properties of $ZnO$. Then, some experimental aspects are aborded about the characterization techniques used along with all the technical details. Finally, results are presented following the process to identify the structural properties as a function of the synthesis parameters.

4.1. State of the art: Structural and morphological properties

Using the sputtering as a synthesis technique, there are several reports of $ZnO$ and a few less about $Co$ doped $ZnO$ [178–180]. During the last few years, it has received great attention to solving the environmental pollutants issues because of its low cost and nontoxic nature [181, 182]. Hammad et al. [183] have successfully shown the change in structural characteristics of $ZnO$ by $Co$ doping, and when no extra peaks were found related to cobalt metal, cobalt oxide, and any other $Zn – Co$ phases, it is suggesting that the doped $Co$ ions are primarily incorporated into the $ZnO$ lattice [180, 184]. The change in the principal $ZnO$ peak shifted towards the higher or lower diffraction angle with the Cobalt concentration is attributed with replacement of $Co^{2+}$ ion of radius (0.56 Å) with the $Zn^{2+}$(0, 60Å) in the $ZnO$ lattice [185–187]. Also, it is reported that the intensities of the peaks planes changed at different Oxygen pressure, which also suggested the incorporation of the $Co^{2+}$ ion with the $Zn^{2+}$ions [182]. Co-doping slightly decreased the lattice parameters of the $ZnO$ nanocrystals, inferring that, the $Co^{2+}$ ions were systematically substituted by $Zn^{2+}$ ions without changing the crystal structure [184, 188, 189]. Also, the FWHM of the $Co$-doped $ZnO$ was found to be narrower than that of the undoped sample, suggesting that $Co$-doping improved
the crystallinity of the ZnO nanostructure \cite{178,189,193}. Cobalt peaks are reported usually in concentrations up to 15\%, where peaks near to 44° are reported \cite{98,194}.

The surface roughness of the reported films was increased with the Cobalt \cite{180}. Formation of islands was observed with the introduction of Co-metal into the ZnO thin films. This is usually attributed to the grain boundary pinning effect \cite{195}. Also, the roughness of the samples increases with the Co target power in sputtering reports \cite{180}. Formation of nanorods by sputtering is reported when the Co concentration increase and a strong dependence of the temperature deposit on these nanostructures \cite{178,196}. Some surface chemical composition of the pure ZnO and Co : ZnO thin films at different watt power have been investigated through XPS survey scan \cite{180}. The carbon detected in these samples is attributed to the surface contamination during the sample transfer from chamber \cite{197}. Higher concentration of Cobalt (> 50 W in the Cobalt target) results in secondary phases detected only by XPS technique \cite{180,195,198,204}.

After this brief report review, it can be concluded that the Co concentration, the substrate temperature, and chemical nature are the most relevant parameters in the structural and morphological properties of the Co : ZnO samples.

\section*{4.2. Experimental aspects}

There are some experimental techniques involved in this chapter: a profilometer to study the thickness of the thin films, an X-ray diffractometer for the structural properties, an Auger spectroscope to study the atomic composition of the samples, and, for the morphological characterization, an electron microscope and an atomic force microscope. Here, the fundamentals of each of these techniques will be briefly explained.

The X-ray diffraction technique consists of a compositional and structural method that allows not only the identification of the composition of mono or polycrystalline material but also its crystalline phases, crystalline structure, preferential orientation, etc. It consists of bombarding a sample with ionizing radiation (highly energetic) at different angles and detecting the reflected radiation from the sample to interpret the angles at which constructive interference exists \cite{205}. X-ray production is a consequence of the deceleration of electrically charged particles \cite{206}. In this case, emission occurs when highly energetic electrons collide against a target given that the kinetic energy of the incident particles is very high. As a consequence, these particles can penetrate the inner energy levels of the atoms present in the target and then displace the electrons located in the K orbitals, therefore, leaving a vacancy on the first energy level, which will be occupied by an electron of the outer orbitals (L or M).

When an electron undergoes a sudden decrease in its energy, dropping from a higher en-
ergy level to a lower energy level inside the atom, a photon with the characteristic frequency of X-ray radiation will be emitted from it, the energy of this photon is characteristic for every material. Once the highly energetic photons are produced, they will pass through a collimator and a monochromator to guarantee that the incident radiation is as coherent as possible; this is important because the diffraction would not be detected from the sample if the incident wave is not in the same phase.

When the X-rays reach the sample, two non-mutually exclusive physical phenomena take place. The first is the emission of X-rays by photonic incidence, and the second one is the X-ray diffraction process. The most relevant physical process in this technique constitutes the X-ray diffraction: every monocrystalline material can be considered as a large set of diffraction slits in which the line division distance corresponds to the distance between two adjacent planes of the crystalline lattice. Once the radiation reaches the planes of the material, these are diffracted at a determined angle; if two waves emitted from the sample are in the same phase, the maximum intensity condition, also known as constructive interference, will be achieved and therefore the detector will receive an abrupt increase in radiation.

The angle at which a diffraction peak is registered depends exclusively on $\theta$, therefore the entire set of angles in a crystal at which diffraction occurs depends only on the dimensional characteristics of its lattice and not on the positions of its atoms [207]. This implies that every X-ray diffraction pattern is characteristic of every material and therefore allows the unequivocal identification and characterization of it. In polycrystalline materials, there will be a higher number of angles at which constructive interference occurs, which results in a diffractogram exhibiting more peaks. In amorphous materials, compositional characterization is not possible with this technique due to a lack of a large-scale periodic structure inside the material, which will not allow the diffraction between planes.

Auger electron spectroscopy (AES) provides compositional information of the first atomic shells, due to the interaction of high-energy electrons with the surface of a material. When an incident electron interacts with an atom, it can generate ionization from an internal level which, when relaxing, fills the vacancy with an electron from an external level. The released energy can be taken up by an electron from the same shell or another outer shell, producing the emission of an Auger electron or emitting a photon [208]. The energy of the Auger electron depends exclusively on the energies of the atomic levels of its host atom. This Auger energy is characteristic of each atom and allows the direct identification of the element, even if the identified Auger electron comes from the valence band [208].

The Auger process is most dominant for kinetic energies below 2000 eV and strongly decreases for higher energies where the fluorescence yield is increasing [209]. Therefore, the most predominant Auger peaks are the KLL transitions for elements with atomic numbers
from 3 to 14, the LMM transitions for elements 14 to 40, and the MNN transitions for the heavier elements \[209\]. Therefore, the line shape of the AES spectra is influenced by plasmon losses \[210\] and ionization loss, so that the ionization loss energy can change by modifying the energy of the primary beam \[209\].

Scanning electron microscopy (SEM) is a handy technique to identify the morphological characteristics of the samples. This technique is based on the theoretical relation proposed by De Broglie in 1924 in which he proved that an accelerated electron beam has an associated wavelength, involving that a potential acceleration of 60 kV or an 80 kV will exhibit wavelengths ranging from 0.005 to 0.0043 nm, respectively. As a comparison, when an optical microscope is used, assuming a wavelength of 500 nm, the limit for resolution is around 217.86 nm \[211\]; in an electron microscope, this value would be enhanced by at least three orders of magnitude, given the fact that the wavelengths of the particles used are 103 times smaller, this proves to show the major advantage of using a scanning electron microscope in material science for the identification of possible surface nanostructures on a sample instead of an optical microscope \[211\].

In a SE microscope, the emission of electrons is from a tungsten filament that is heated using an electric current which consequently emits electrons that are then accelerated using electric tension ranging typically from 5 kV to 30 kV; the temperature at which the filament starts the thermionic emission is around 2700 K, if a greater current is put through the filament, a greater number of electrons will be obtained, however, it may compromise the mean life of the filament.

The entire system must have high vacuum conditions \(< 1mPa\) for the mean free path of the electrons to be enough to reach the surface of the sample. An increase in resolution is achieved by focusing the electrons in an extremely thin beam, which is made employing copper lenses along the column. Once the electrons reach the sample, they begin to interact with its surface causing several physical phenomena and particle emission \[212\], the latter process is of great importance for the morphological characterization because the emitted particles are the ones responsible for the obtaining of the micrographs. Here, three important emitted particles are relevant: secondary electrons, backscattered electrons, and characteristic X-Rays photons.

The secondary electrons are the particles ejected from the outermost regions of the material under study, these are valence electrons from the atoms that are ripped from them once the energy of the incident electron beam overcomes the ionization potential of an atom. Given the fact that these are low energetic particles \(\text{inferior to } 50 \text{ eV}\), only the outermost electrons can be emitted from the sample. After emission takes place, these electrons are detected by the secondary electron detector coupled with a photomultiplier and an amplifier
that translate the different intensities into an image on a computer. These electrons are useful for the study of surface topography.

Backscattered electrons are particles directly coming from the incident beam, but reflected after interaction with the surface of the sample, changing energy. These are reflected from deeper regions of the sample, not only from its surface, and are more sensitive to the chemical composition of the sample: The greater the atomic number (Z) of an atom inside the material, the greater the quantity of emitted backscattered electrons; therefore, given that the detector assigns a different brightness to different received intensities, the areas with heavier elements will appear brighter in a micrograph, whilst the areas with smaller Z numbers will appear more opaque. The detector of backscattered electrons allows not only a topographical, but also a compositional study of the sample.

The characteristic X-ray photons are emitted by the standard process, when an incident electron beam interacts with a sample, this radiation is captured by an X-ray detector and allows the compositional characterization of the material employing the energy-dispersive X-ray spectroscopy (EDXS) technique. The interacting layers in this process depend on the energy of the incident beam, and if the sample is too thin, there can be some overlapping with the substrate composition.

Atomic force microscopy (AFM) is a technique for topographic and morphological characterization. It works under the physical phenomena of electrostatic repulsion and Van der Waals attraction and it reaches atomic resolution. The measuring process consists basically of scanning the surface of the sample with a probe placed on a cantilever (at a 10 Å separation), detecting any change in its surface through the movement of a light beam coming from a laser, whose reflection from the cantilever points towards a photo-detector that allows the collection of the feedback of the topography in the material. The probe is usually made of silicon nitride ($\text{Si}_3\text{N}_4$), and the cantilever itself generally is made of pure silicon. An ideal probe should be one atom thick to guarantee a perfect resolution, however, commercial probes have lengths of around 3 to 6 µm with a radius of 15 to 40 nm, which still imply resolutions of up to 0,1 nm. It can operate in three separate modes: Contact mode, non-contact mode, and tapping mode [213].

The tapping mode is the middle point between contact and non-contact modes; when the contact mode is applied to a sample, the tip oscillates all over its surface at small amplitude, however in this process, because of the adhesive forces of the material under study, the tip may result contaminated and the measurement distorted. The tapping mode eliminates this disadvantage because the tip is intermittently in contact with the surface and it oscillates with enough amplitude to prevent the tip from getting trapped under said adhesive forces. The result is that this mode provides the best resolution with minimum damage to the sam-
ple; in most cases, the non-contact mode is operated as a tapping mode instead.

There are other additional microscopy modes, changing the chemical nature of the tip, that can be configured into AFM equipment to evaluate other characteristics of a material, for example, evaluate the presence and distribution of magnetic domains in the surface of a sample.

Profilometry is a technique used to extract topographical data from a surface. This can be a single point, a line scan, or even a full three-dimensional scan. The purpose of profilometry is to get surface morphology, step heights, and surface roughness. This can be done using a physical probe or by using light. Stylus profilometers use a probe to detect the surface, physically moving a probe along the surface to acquire the surface height. This is done mechanically with a feedback loop that monitors the force from the sample pushing up against the probe as it scans along the surface. A feedback system is used to keep the arm with a specific amount of torque on it, known as the 'setpoint'. The changes in the Z position of the arm holder can then be used to reconstruct the surface.

4.3. Methods and model

The samples were characterized from XRD measurements using X-ray diffractometer X'Pert Pro polycrystal PANalytical, equipped with a source of \( Cu - K_{\alpha1} \), a potential difference of 40 kV, current of 40 mA, and X'Celerator detector. The software used to compare the samples was X'Pert HighScore Plus. The thin film thickness was studied using a Dektak 150 from Veeco. This is a surface profilometer that takes surface measurements using contact profilometry techniques in a line. This is equipped with a Low-Inertia Sensor (LIS 3) using a 3 mg force on the 10 nm stylus. It has a resolution of 10 Å in the 10 µm range where was set up. For the morphological characterization of the samples were used an electron microscope (SEM) Vega3 SB with tungsten source, an XFlash Detector 410 M, and an acceleration voltage of 10 kV under high vacuum (\( \sim 10^{-5} \) Pa) and Atomic Force Microscopy (AFM) Asylum Research MFP 3D Bio in tapping mode, the magnetic-domain investigation was carried out by using this same AFM in MFM mode on the surface of the sample using a Co tip. This measurement allows both the topographic and the magnetic-force image to be collected separately. Additionally, the SEM microscope has an X flash 410 M detector and SDD for EDXS microanalysis. Auger measurements were performed in an AES Omicron spectroscope. With a tungsten gun to bombard energetic electrons in the 2 – 50 KeV range under ultra-high vacuum conditions (\( \sim 10^{-8} \) Pa). The Argon gun to clean the surface and go into the bulk was set-up in \( xx \) mA for \( yy \) s. In this chapter, all the mentioned characterization techniques were performed at room temperature. All the fitting were performed using the least-squares method with a Levenberg Marquardt algorithm. Also, SEM micrographs were treated using Python 2.7. Here a Contrast enhancement was executed with a 0,5% of tolerance.
4.4 Results and discussions

Before all else, due to the sputtering chamber configuration, the Cobalt distribution in the substrates (Fig. 2-1b) depends on the substrate position. Through EDXS measurements the relative Cobalt concentration in each sample position was identified. Following that, the sputtered particles follow a free mean path until reaching the substrate, which interrupts the trajectories into a conic section. Also, it is known by the experimental measurements that the Co concentration is greater near to the Co-target and lower close to the ZnO-target. So, based on a few EDXS measurements in different substrates, interpolating can be determined the Co distribution in the samples. Through a basic 4th order algorithm, and strained to the physical constraints, the relative percentage of Cobalt atoms with respect to Zinc atoms was founded. Fig. 4-1 shows this results in a contour plot-oriented according with the Fig. 2-1b.

Figure 4-1.: Contour plot of the relative Cobalt atomic concentration as a function of the localization in the substrate holder.

Once the Cobalt concentration was determined, the next thing studied was the thickness of the thin films. Physically it is expected that the number of sputtered particles increases with the time of deposit. Due to the substrate distribution in the chamber, it depends on
the position of the substrate. With a profilometer, some samples with different deposit times were measured. The needle-height was recorded, and when it passes over the interface, thin-film/substrate, a significant change was observed (Fig. 4-2a).

The results were fitted using a linear fit before and after the interface. The height difference in the midpoint corresponds to the thickness of the thin film. This process was iterated in the rest of the samples. The thickness showed a tendency with the time deposit as expected (Fig. 4-2b). Also, the fact that it is not linear has a lot of sense, due to the nature of the synthesis. So, a logarithm function could explain the growth as a function of the deposit time. The thickness of the samples over ITO have similar behavior, but in this case, for the same deposit time, there is a lower value for the thickness. That could be explained due to the chemical nature of the substrate, which allows the sticking of a higher number of sputtered atoms during the synthesis. Here the Cobalt concentration is possible evidence of this, the samples over Si have a higher concentration of Cobalt, with the same target power, so perhaps due to the chemical nature and the structural similarity, there are more ZnO and Co atoms in the sample over Si than in the sample on ITO. Also, some authors report a decrease in the in-plane constant of ZnO when Cobalt is added, while the lattice out-plane constant increases [214]. So, a higher concentration of Cobalt can result in a macroscopic increase in thickness. The thickness of the samples is an important value for the next characterization techniques, which involve knowing its value for the models, or the experimental setup.

Figure 4-2.: (a) Profilometer results of a ZnO thin film sample in its interface. (b) ZnO Thickness as a function of the deposit time for two different Co concentration, with a Ln-like fit.
The biggest problem for the Cobalt distribution determined by EDXS measurements is that we have a superposition with the contributions from the substrate, and it is pretty complicated to separate it from the sample. As it was studied in the previous chapter, the Oxygen vacancies play a relevant role in the physical properties of the $ZnO$. Even with the beam-energy is lower, there is saturation in the measurement from the substrate contribution, due to the nanometric thickness of the thin films. There are several superficial techniques, but we are interested in the atomic composition of the bulk, without reach the substrate. To solve this, a variation of the Auger spectroscopy was used (See Fig. 4-3).

![Fig. 4-3](image)

Figure 4-3.: Auger spectroscopy results for $ZnO$ thin films synthesized at different $P_{Co}$.

Here, there is an Argon gun that cleans the surface to avoid dirtiness. But, also it can sputter the surface to measure deep in the bulk. So, the Ar-gun clean the surface and take another measurement. That was repeated until the substrate was reached. After 12 measurements the Auger spectrometer detects the substrate. The spectra were analyzed to identify and quantify the contribution of the atoms. Fig. 4-3 shows the results of the spectroscopy. A total of 14 different peaks were identified, included one for C (superficial dirt) and Si.
Structural and morphological characterization of Cobalt doped ZnO (substrate). For the peak identification, in C++ was developed an algorithm, where also was performed the quantification method. This software also identified the associated triple-transition.

In Fig. 4-3 are shown only a few spectra, only for visualization reason. The down-arrows indicate the profundity in bulk, i.e., the lower spectra are closer to the substrate. Fig. 4-3a does not present any Cobalt peaks due to the absence of Cobalt in the synthesis. The Co peaks in Fig. 4-3b, 4-3c, and 4-3d are not equal in relative intensities in each measurement, this is a clue for a random located ions. Also, there are some slight variations in the Co, Zn, and O positions, as a trace of different kinds of bounds (share electrons). The average results of the quantification process are shown in Fig. 4-4.

Figure 4-4.: Average atomic composition of the Co:ZnO thin films through Auger spectroscopy for samples synthesized with (a) $P_{Co} = 0$ W, (b) $P_{Co} = 20$ W, (c) $P_{Co} = 40$ W, and (d) $P_{Co} = 60$ W.

The relative values of the Cobalt concentration are 8, 7 ($P_{Co} = 20$ W), 13, 18 ($P_{Co} = 40$ W) and, 14, 38 ($P_{Co} = 60$ W). So, as expected the relative concentration (and the absolute) increase with the power of the Co-target. Also, it is remarkable that the ratio of atoms $O:Zn$ is on average 0.49. It implies that there are a lot of Oxygen vacancies in the structure, and possible Zn clusters. Even in this prospect, from the previous chapter, it is known that there is more likely a double $VO$ than a $COO$ substitution.

Now that the concentration of Cobalt was established and it was identified a relation of like two Zn atoms per each O, i.e. an absence of O in the deposit process, XRD measurements were performed. In this step, the influence of $P_{Co}$ is clear. Remembering that DMS materials need no magnetic clusters, it is necessary to find a balance between the magnetic response and the non-presence of Magnetic crystal phases. Also, possible Zn clusters could reduce the semiconductor properties.
Considering the synthesis parameters, there are three relevant variables in the crystal structure of the thin films: the chemical nature of the substrate, thermal stimulation, and Cobalt concentration. In the first aspect, we choose some substrates for its minimal coincident interface area (MCIA) and elastic energy with the Wurtzite ZnO \[215\]. These substrate were Au (0.060 meV and MCIA=121.8), \(SiO_2\) (0.074 meV and MCIA=192.0), and \(Al_2O_3\) (0.096 meV and MCIA=180.0). Fig. 4-5 shows the diffraction patterns for ZnO thin films over those substrates and soda-lime glass. These samples were fabricated at 423(2) K with \(P_{Co} = 40\) W. Some peaks in Fig. 4-5 are matched to the substrate, and just slight variations in intensity, FWHM, and central position are observed. These variations are attached to the growth of the ZnO on the substrate preferential planes.

Peaks 1-13 in 4-5 are identified in Table 4-1. There also are presented the corresponding PDF file, the diffraction plane, the crystal system, and the space group. At the end of the table 4-1, two extra peaks are presented. These corresponding to the \(Al_2O_3\) principal peak and the \(Si\) peak of orientation. The first one is difficult to see because the atomic form factor of the closest \(Al\) peak is too much bigger. Concerning the second extra peak, probably the oxidation process and the amorphous \(SiO_2\) film over the \(Si\) produce a destructive interference and make it impossible to see. But it corresponds to the growth plane provided by the Si manufacturer (See Appendix B).
Table 4-1: Identified peaks in Fig. 4-5 for substrates and Co doped ZnO thin films.

<table>
<thead>
<tr>
<th>#</th>
<th>Pos. [2θ°]</th>
<th>Match</th>
<th>PDF file</th>
<th>Plane</th>
<th>Crystal system</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34,364</td>
<td>ZnO</td>
<td>01-080-00074</td>
<td>002</td>
<td>Hexagonal</td>
<td>186</td>
</tr>
<tr>
<td>2</td>
<td>36,207</td>
<td>ZnO</td>
<td>01-080-00074</td>
<td>101</td>
<td>Hexagonal</td>
<td>186</td>
</tr>
<tr>
<td>3</td>
<td>38,185</td>
<td>Au</td>
<td>00-004-0784</td>
<td>111</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td>4</td>
<td>38,473</td>
<td>Al</td>
<td>00-004-0787</td>
<td>111</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td>5</td>
<td>44,393</td>
<td>Au</td>
<td>00-004-0784</td>
<td>200</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td>6</td>
<td>44,140</td>
<td>Al</td>
<td>00-004-0787</td>
<td>200</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td>7</td>
<td>62,754</td>
<td>ZnO</td>
<td>01-080-00074</td>
<td>103</td>
<td>Hexagonal</td>
<td>186</td>
</tr>
<tr>
<td>8</td>
<td>64,578</td>
<td>Au</td>
<td>00-004-0784</td>
<td>220</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td>9</td>
<td>65,135</td>
<td>Al</td>
<td>00-004-0787</td>
<td>220</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td>10</td>
<td>69,119</td>
<td>SiO₂</td>
<td>01-085-0461</td>
<td>300</td>
<td>Hexagonal</td>
<td>154</td>
</tr>
<tr>
<td>11</td>
<td>75,967</td>
<td>SiO₂</td>
<td>01-085-0461</td>
<td>104</td>
<td>Hexagonal</td>
<td>154</td>
</tr>
<tr>
<td>12</td>
<td>77,549</td>
<td>Au</td>
<td>00-004-0784</td>
<td>311</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td>13</td>
<td>78,230</td>
<td>Al</td>
<td>00-004-0787</td>
<td>311</td>
<td>Cubic</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>37,763</td>
<td>Al₂O₃</td>
<td>01-077-2135</td>
<td>110</td>
<td>Rhombo.</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td>46,384</td>
<td>Si</td>
<td>00-035-1158</td>
<td>200</td>
<td>Cubic</td>
<td>225</td>
</tr>
</tbody>
</table>

*See Appendix C.*

The principal peak of ZnO (2θ = 34, 364°) corresponds to the Wurtzite phase (plane [100]). This phase has an elastic energy/MCIA with each substrate of 0.016 meV/28 Å² ([111] Al), 0.096 meV/180 Å² ([100] Al₂O₃), 0.060 meV/121 Å² ([111] Au), and 0.074 meV/192 Å² ([110] SiO₂). Also the [110] Si plane has 0.055 meV/239 Å² with the [100] Si.

The next relevant variable in the structure of the Co: ZnO is the Cobalt concentration. If it is too high, clusters of Cobalt will start to form, as well as secondary phases of CoₓOᵧ. If the Cobalt atoms are well distributed in the semiconductor matrix, no-extra diffraction peaks will appear. But, the presence of the impurities atom distorts the structure, and consequently the peaks in the diffraction pattern. This distortion could appear as a shift of the ZnO peaks, a change of the FWHM, a change in the relative intensities, and destruction of peaks. Fig. 4-6 and Fig. 4-7 show XRD measurements for the samples prepared with different P_Co (0 W, 20 W, 40 W, and 60 W).
4.4 Results and discussions

Figure 4-6.: X-ray diffraction pattern of the $Co:ZnO/Al_2O_3$ samples synthesized at different Cobalt target power.

Figure 4-7.: X-ray diffraction pattern of the $Co:ZnO/Si$ samples synthesized at different Cobalt target power.

There are not new peaks in the patterns when the Cobalt is added, even in the highest $P_{Co}$, and the variations in the pattern are imperceptible. Table 4-2 shows the original values for $P_{Co} = 0$ W, the changes in the peak position, and the FWHM. Also, Table 4-2 shows the relative intensities with the principal peak of each pattern for the $Zn[100]$ peak and the relative change in the intensity of the principal peak.
Structural and morphological characterization of Cobalt doped ZnO

There is no apparent relation between the increase of Cobalt and the FWHM, or the relative intensities. Nevertheless, the change in the position decreased when \( P_{Co} \) increased. So, there is a first strong change in the position, and then it is smaller as the impurities increase. Probably that is a result of the formation of segregated phases of Cobalt. These phases are no-showed in XRD measurements due to their low concentration in the sample and their segregated nature. Some authors report several peaks associated to the different Co form into the material (\( \text{Zn}_{1-x}\text{Co}_x\text{O}, \text{Co}_3\text{O}_4, \text{ZnCo}_2\text{O}_4 \)) \[214, 216\]. All these peaks are near to 36° and the assignment is nontrivial, tiny shifts to the lower angles of the principal \( \text{ZnO} \) peak (\( \sim 36° \)) may be assigned to \( \text{Zn}_{1-x}\text{Co}_x\text{O} \), where the Cobalt is replacing a Zinc atom in the structure. That is the case of the samples with different Co concentrations, and since no return to the original position is observed, it can be concluded that no Co phases are present in a notable quantity. On the other hand, the most common Co phase, which is possible in the synthesis condition, is characterized by a remarkable peak near to \( \sim 44° \) and a decrease in the intensity of the \( \text{ZnO} \) peaks while that peak increase \[214\]. That is another reason to think that no secondary phases are present in thin films.

The final aspect that might affect the structure of the \( \text{Co : ZnO} \) is the deposit temperature. Despite having an \textit{in situ} annealing process at 473(2) K for two hours, and lower temperatures in the synthesis, we expect that there has some influence. This temperature influence in the structure could be due to the species mobility when the film is growing. We expect to observe some dependence of the Co diffusion with the temperature. Fig. 4-8 and Fig. 4-9 show the diffractogram of samples prepared at different temperatures (\( T_s = 293(4), T_s = 323(6), T_s = 373(3), \), and \( T_s = 423(2) \)) on \( \text{Al}_2\text{O}_3 \) and \( \text{Si} \) respectively.

Table 4-2.: Principal peaks position, FWHM, and relative intensities values/changes extracted from the XRD patterns of the \( \text{Co : ZnO} \) samples synthesized at different powers for the Cobalt target.

<table>
<thead>
<tr>
<th>( P_{Co} ) (W)</th>
<th>Substrate</th>
<th>Position ( (2\theta^o) )</th>
<th>FWHM ( (2\theta^o) )</th>
<th>R. Intensity ( (%)</th>
<th>Position ( (2\theta^o) )</th>
<th>FWHM ( (2\theta^o) )</th>
<th>R. Intensity ( (%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>38,50</td>
<td>0,12</td>
<td>100,00\textsuperscript{b}</td>
<td>34,36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>-0,05\textsuperscript{a}</td>
<td>-0,03\textsuperscript{a}</td>
<td>151,70\textsuperscript{b}</td>
<td>0,07\textsuperscript{a}</td>
<td>0,52\textsuperscript{a}</td>
<td>4,62\textsuperscript{c}</td>
</tr>
<tr>
<td>40</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>-0,01\textsuperscript{a}</td>
<td>-0,09\textsuperscript{a}</td>
<td>97,38\textsuperscript{b}</td>
<td>0,05\textsuperscript{a}</td>
<td>0,45\textsuperscript{a}</td>
<td>10,98\textsuperscript{c}</td>
</tr>
<tr>
<td>60</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>-0,02\textsuperscript{a}</td>
<td>-0,03\textsuperscript{a}</td>
<td>91,98\textsuperscript{b}</td>
<td>0,04\textsuperscript{a}</td>
<td>0,55\textsuperscript{a}</td>
<td>10,26\textsuperscript{c}</td>
</tr>
<tr>
<td>0</td>
<td>( \text{Si} )</td>
<td>68,51</td>
<td>5,20</td>
<td>100,00\textsuperscript{b}</td>
<td>33,62</td>
<td>0,98</td>
<td>91,13\textsuperscript{c}</td>
</tr>
<tr>
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<td>( \text{Si} )</td>
<td>-0,59\textsuperscript{a}</td>
<td>0,19\textsuperscript{a}</td>
<td>56,65\textsuperscript{b}</td>
<td>-0,69\textsuperscript{a}</td>
<td>0,62\textsuperscript{a}</td>
<td>425,22\textsuperscript{c}</td>
</tr>
<tr>
<td>40</td>
<td>( \text{Si} )</td>
<td>-0,55\textsuperscript{a}</td>
<td>0,10\textsuperscript{a}</td>
<td>89,16\textsuperscript{b}</td>
<td>-0,63\textsuperscript{a}</td>
<td>0,16\textsuperscript{a}</td>
<td>28,18\textsuperscript{c}</td>
</tr>
<tr>
<td>60</td>
<td>( \text{Si} )</td>
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<td>-0,44\textsuperscript{a}</td>
<td>74,38\textsuperscript{b}</td>
<td>-0,52\textsuperscript{a}</td>
<td>-0,12\textsuperscript{a}</td>
<td>29,47\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\( a \) \( P_{Co=0} - P_{Co} \) \hspace{1cm} \( b \) \( P_{Co}/P_{Co=0} \) \hspace{1cm} \( c \) \( P_{100}/P_{1st} \)
4.4 Results and discussions

Figure 4-8.: Diffractogram for the Co doped ZnO samples over Al₂O₃ prepared at different substrate temperature.

Figure 4-9.: Diffractogram for the Co doped ZnO samples over Si prepared at different substrate temperature.

There are the same peaks when the synthesis temperature change. Once again, the changes are more about the characteristics of each peak. Table 4-3 shows the original values for $T_s = 293$ W, the changes in the peak position, and the FWHM. Also, Table 4-3 shows the
relative intensities with the principal peak of each pattern for the Zn[100] peak and the relative change in the intensity of the principal peak.

A new, seems like there are no evident correlation in the relative intensities. In the samples over Si, the FWHM increases when the $T_s$ does it. Also, the Zn[100] peak position has a left-shift that increase with $T_s$. There are no major changes in the diffraction patterns in the studied range when the synthesis temperature increase. It is probably because the posterior in situ annealing has a higher temperature, so, the maximum mobility of ions is set by that temperature.

Another feature that might change with the deposit temperature is the topography of the samples. Due to the higher atoms’ mobility when the temperature increase, there are more and bigger grains. The thin-films formation can be resumed as a four-step operation. A stochastic process of nucleation first. Then a controlled growth by the surface diffusion of the three-dimensional nuclei. Next, the formation of a network structure. And, finally, a subsequent filling to achieve a continuous film. Depending on the thermodynamic parameters of the deposit and the substrate surface, the initial stages of nucleation and growth can be described in three ways. (a) island type, called Volmer-Weber type, (b) layer type, called Frank-van der Merwe, and (c) mixed type, called Stranski-Krastanov type. In almost all practical cases, growth is produced by the formation of islands [217].

Fig. 4-10 shows comparative results between a sample synthesized at room temperature (293 K) and another at 373 K.
4.4 Results and discussions

Figure 4-10: SEM micrographs of Co : ZnO/Ti thin films fabricated at 293(4) K (left) and 373(2) K (right). All micrographs are from SE at $HV = 30$ kV, average $WD = 10.05(1)$ mm and magnifications of 10kx (a, b), 20kx (c, d), and 40kx (e, f).

The micrographs have some slight differences at 10kx. The room-fabricated have more fissure than the other. Probably cause there is more species mobility at higher temperatures. Also, due to the thermal stimulus more sputter atoms stick to the substrate. In conclusion, there are more atoms with higher mobility when the substrate temperature increase. So, that results in a more homogeneous thin film.

The chemical nature of the substrates is an important factor in the morphology of the thin films. That is due to their low thickness, so the first nanometers try to reproduce the substrate morphology. Also, the species mobility is bounded to the free bonds and electronegativity of the substrate surface. Fig. 4-11 shows comparatives micrographs synthesized on the different substrates.

The dependence of the substrate in the morphology is evident. There are some islands in the sample over Ti (Fig. 4-11a) as we see in above (Fig. 4-10). Some black points are present on Co : ZnO/Au (Fig. 4-11b), but seems homogeneous under that. The film deposited over glass is the most uniform (Fig. 4-11c), also is the micrograph at lowest $HV$ due to the insulator characteristic of the soda-lime glass. Some grains are observed in the Co-doped films over ITO (Fig. 4-11d) and $Al_2O_3$ (Fig. 4-11e), being smaller in the second one. Finally, there are some grooves on the sample over Si that seem like the trace of bigger island formation.
Structural and morphological characterization of Cobalt doped ZnO

Figure 4-11: SEM micrographs of Co : ZnO thin films fabricated at 423(2) K over Ti (a, g), Au (b, h), soda-lime glass (c, i), ITO (d), Al₂O₃ (e, j), and Si (f). All micrographs are from SE at HV = 30 kV (except c and i at 10 kV), average WD = 9.8(1) mm and magnifications of 10kx (a, b, c, d, e, f), 20kx (h, j), 36kx (i), and 40kx (g).

Now we are interested in the effect of Cobalt in the morphology, but in the resolution of the SEM apparently, there are not variations. So, AFM micrographs were taken in samples with different Co concentrations. Also, AFM can be performed in different modes. Using a Co tip, the magnetic interaction between an induced magnetic moment in the tip and the sample can be recorded. This extra-measurement gives information about the magnetic distribution in the surface, like magnetic domains. Fig. 4-12 show some AFM/MFM micrographs as a function of the $P_{Co}$.

The grain height increase significantly when the Cobalt increase in the semiconductor matrix. It is easy to observe in the change of the scales, where the range change from 8.5 nm ($P_{Co} = 0$ W) to 180 nm ($P_{Co} = 60$ W). Also, the intensity of the magnetic response is bigger.
Zoom in Fig. 4-12 b and its 3D representation (Fig. 4-12 c) show an isotropic distribution of the grains. That is very important to industrial applications. If the grain distribution would have a spatial dependence, there would have no standard electric properties, but as expected the sputtering technique results in uniform films.

Figure 4-12.: AFM/MFM micrographs of ZnO (a-c) and Co-doped ZnO. Thin films prepared over soda-lime glass at 423(2) K and $P_{Co} = 20$ W (d-f), $P_{Co} = 40$ W (g-i), and $P_{Co} = 60$ W (j-l). All the color-bars scale are in nm. Gold figures AFM Height, and cold-warm scale represent the amplitude of the signal from the magnetic interaction. Z-axis in 3D plots represent the AFM height.

Comparing Fig. 4-12 e and Fig. 4-12 f (Zoom of the Fig. 4-12 d) there is some correlation in the highs of the topographic and magnetic response. From here it can be inferred that the grains have a high concentration of Co. The spintronic application requires maintaining the semiconductor properties of the samples, if the grain boundary is too well defined it
may represent a problem. Possible Co phases are present in these grains, and there is not a uniform distribution of Cobalt on the surface. In a similar way, Fig. 4-12g and Fig. 4-12h have a correlation, and the 3D-zoom (Fig. 4-12i) helps to understand it. Here, the grain is more defined but it is only one of it in 25µm². o, there is no reason to worry about it if we keep a higher scale in the applications. The worst scenery is to have extensive and high grains with a stronger magnetic response. Unfortunately, is the $P_{Co} = 60$ W case. There, no secondary phases were identified by XRD measurements, but huge magnetic grains are on the surface (See Fig. 4-12j-l).

Now, the primordial interest is to have a balance between the magnetic response and the no-Co-phases condition. Although the grains are not necessarily evidence of secondary phases, if it does not exist there are not concerns. The AFM measurements allow the quantification of how high are in average the grains in the sample. This is known as roughness. Besides the roughness, the root-mean-square (RMS) roughness (Rq) is the square root of the distribution of surface height (See Fig. 4-13).

Figure 4-13.: Root mean square roughness as a function of the Cobalt power target for $Co : ZnO$ thin films synthesized at 473(2) K over soda-lime glass. Error bars represent the standard deviation.
4.4 Results and discussions

It is considered to be more sensitive than the average roughness for large deviations. In the Fig. 4-12 cases, there are some isolated big grains. So, RMS is the best option. The Fig. 4-13 shows that value as a function of the $P_{Co}$. Here, a logarithmic scale is necessary cause the variation in the RMS from 40 W to 60 W is more than 600%. Here there is a huge change in the topography and the magnetic response. In the figure can be observed a change even in the concavity of the tendency. In the magnetic RMS, the change is also large, but in $P_{Co} = 0$ there is no data. That value can be assumed very close to 0 pm, but once again would be another outsize change. Focus on that, when we have no Cobalt in the semiconductor matrix, we do not have a DMS. Also, when we have too much Cobalt in the structure, it becomes an alloy and stops being a DMS. In that logic, the $Co$ concentration appears to be an order parameter.
5. Electrical, optical and magnetic characterization of Cobalt doped ZnO thin films

Until now, Cobalt concentrations were identified for different $P_{Co}$ values and their distribution on the substrates. Also, there are no secondary phases of Co presented in the XRD analysis. Finally, it was identified a strong correlation between the M-RMS and the Co concentration. Now, the principal interest is to correlate the optical, electrical, and magnetic properties of the thin films with those results. To do that, this chapter starts similarly to the previous. First, a background is seated and after establishing the experimental and technical details the results of the optical, electric, and magnetic characterization are presented.

5.1. State of the art: Electrical, optical and magnetic properties

To develop information storage devices, both magnetic and electrical properties of solid-state materials have been considered, including magnetic recording, magnetoresistive random access memory (MRAM), and flash memory, resistive random access memory (RRAM) [218]. In these techniques, the spin, and charge of electrons are employed separately. Transition metal-doped ZnO is a promising candidate material for the field of spin-electronics.

Carrier spins are used to transport, store and process information in novel ways, providing both enhanced performance and new functionalities in traditional microelectronic devices. The magnetic properties of a DMS are intimately coupled to the carrier concentration and carrier type within the material through the s–d and p–d exchange integrals. This is beneficial because it allows external control over the magnetic properties by electronically or optically manipulating the carriers in the DMS [219,220]. For example, in magnetic recording, a magnetic field is used to write or read the information stored on the magnetization. Simultaneously, RRAM, as a promising candidate for next-generation nonvolatile memory, is based on resistance change (high and low) modulated by an electrical stimulus, for the recording of two logic states (“0” and “1”) [221]. The quest for higher data density in information storage is motivating research on manipulating magnetization without the need
5.1 State of the art: Electrical, optical and magnetic properties

of H. to achieve a new paradigm where spin and charge act on each other. Ultimately, allowing faster, low-energy operations with a combination of information writing, transfer, treatment, and reading. RRAM is currently of great interest to realize the switching between insulating/conductive states with an ultrahigh off/on ratio. Cobalt-doped ZnO ($\text{Co}:\text{ZnO}$) has been selected as the storage medium in this work for three reasons. First, $\text{Co}:\text{ZnO}$ stands out as a seminal spintronic material due to its high TC. Second, $\text{Co}:\text{ZnO}$ shows robust ferromagnetism under both insulating and metallic states. At last, the ZnO commutation systems show stable RS during repeated sweep cycles.

Dietl’s theory is based on an indirect exchange mechanism where the ferromagnetism between magnetic dopants is mediated by holes in the valence band. P-type material was predicted to result in high TC primarily because both the exchange integral parameter and the density of states are higher in the valence band than the conduction band. Dietl’s theory has proven useful in understanding the experimental results for $\text{GaMnAs}$. However, it does not appear to be consistent with the experimental results for transition metal-doped wide bandgap semiconductors, such as ZnO and GaN. This stems from several reasons, including the difficulty in experimentally preparing p-type ZnO material and the many observations of ferromagnetism in n-type ZnO DMS. Nevertheless, Dietl’s original theory has led to multiple experimental and computational studies of transition metal doping in ZnO and GaN.

Coey et al. have proposed another model for ferromagnetism in DMS materials based on a spin-split donor impurity band. This model provides a mechanism where ferromagnetism is influenced by defect states in the material. In the model, donor defects (which could arise from either Oxygen vacancies or Zinc interstitials in the case of ZnO) overlap at large concentrations to form an impurity band. The impurity band can interact with local magnetic moments through the formation of bound magnetic polarons (BMP). Within each BMP, the bound carrier interacts with the magnetic dopants inside its radius and can align the spins of the magnetic dopants parallel to one another. Ferromagnetism is achieved when the BMPs start to overlap to form a continuous chain throughout the material, thus percolating ferromagnetism in the DMS. However, Coey showed that, in this model, to achieve a high Tc a fraction of the polaronic charge must delocalize (or hybridize) onto each magnetic dopant. In a band scheme, this occurs when the impurity band overlaps with unoccupied d-levels of the magnetic dopant.

Within a similar framework to Coey’s model, Kittilstved et al. have performed detailed spectroscopic experiments on Cobalt-doped ZnO. Their results show that the singly ionized Co$^+$ state lies close to the conduction band, similar in energy to a shallow donor state. Since the energies are similar, charge transfer (CT) can occur between the Cobalt
atoms and the donor impurities, thus leading to the hybridization necessary for ferromagnetism. Kittilstved et al have also shown that this leads to an inherent polarity difference for ferromagnetism in Cobalt- and Manganese-doped ZnO. Whereas ferromagnetism in Cobalt-doped ZnO is closely tied to the presence of shallow donors, Manganese-doped ZnO is closely tied to the presence of shallow acceptors. The difference lies in the location of the singly ionized Mn+3 state, which sits close to the valence band in ZnO. Consistent results have been reported for carrier-doped Mn:ZnO films [239,240].

Other studies have also elucidated the importance of carriers and defects in mediating ferromagnetism in ZnO. Tuan et al [99] found that weak ferromagnetism in Co-doped ZnO films can be activated by post-growth vacuum annealing, changing the films from insulating to semiconducting behavior. The specific role of Zn interstitials has also been studied. Zn interstitials are believed to form a shallow donor state in ZnO. Reversible on/off ferromagnetic ordering at room temperature in chemically synthesized Co-doped ZnO films was achieved by the controlled incorporation and removal of Zn interstitials [241]. Zn interstitials were introduced by annealing in the presence of Zn vapor and subsequently removed by annealing in Oxygen. The interstitials were believed to activate ferromagnetism by introducing electrons, which were removed by oxidation. Khare et al [242] have also investigated the role of Zn interstitials.

They also found that the magnetization in Co-doped ZnO is enhanced by introducing Zn interstitials into the lattice during annealing, but that the magnetization did not depend on carrier concentration. Their results also indicated that Oxygen vacancies were not responsible for changes in magnetization. However, recent theoretical modeling does suggest that Co+2-Oxygen vacancy pairs are capable of promoting long-range FM coupling in the presence of n-type doping [243]. It seems, therefore, the recent literature suggests that ferromagnetism in Co-doped ZnO is highly dependant on intrinsic defects in the material. These defects may rely on the presence of the transition metal dopants by the formation of complexes that mediate FM ordering or defects alone may be enough to cause ferromagnetism.

The sharp absorption edge and high optical transmission within the visible region of the spectrum are reported as proof of the high quality of ZnO nanostructures. When the samples exhibited sharp absorption near the bandgap edge, indicating that no extra phases are formed [178]. Many groups have confirmed that Co atomically substitutes on Zn sites using a variety of methods, including EXAFS [125,130], XPS [90,99,244,245], MCD [99,234,246], XAS [125,247], ESR [248], XANES [249] and optical absorption [99,101,246,250,251]. Three absorption peaks are reported in the doped films, characteristic of a d–d transition levels attributed to Co+2 occupying tetrahedral lattice positions, and indicate that Cobalt is substituting as Co+2 on Zn lattice sites in the films; these peaks are reported in multiple publications on Zn1–xCo2O films as mentioned above.
Some reports in the literature observe a red-shift in the bandgap energy as the Cobalt concentration is increased [252–255]. The red-shift is typically attributed to the sp–d exchange between the ZnO band electrons and localized d-electrons associated with the doped $\text{Co}^{+2}$ cations. The interaction leads to corrections in the energy bands; the conduction band is lowered and the valence band is raised causing the bandgap to shrink [256]. On the other hand, other papers have reported a blue-shift in the bandgap of ZnO with Cobalt doping. Peng et al [257] reported a blue-shift in the bandgap of the material and a red-shift in the band tails. Ozerov et al [248] also reported a blue-shift in the bandgap in nanocrystalline films. Yoo et al [258] observed a blue-shift in Al- and Co-codoped ZnO films which were attributed to the Burnstein–Moss effect from an increase in the carrier concentration.

5.2. Experimental aspects

In this section some fundamentals of the techniques involved will be approached, this will allow a better understanding of the results. First, an explanation of the Wenner method and its implementation for the thin films, then a simple review of the UV-VIS-NIR spectroscopy is presented, and finally, some generalities of the vibrating sample magnetometer (VSM) used for the magnetic characterization are explained.

The Wenner method [259], also known as the four-point method, consists of obtaining a potential difference and the imposition of a current from 4 electrodes on the surface of the material, in an aligned and equidistant way [259], bearing in mind that conduction can occur superficially, the closer the electrodes are, the less electronic noise the signal will have. Knowing the distance between the electrodes, the applied current, and the potential drop, it is possible to determine the resistivity of the material [259,260].

That configuration allows the measurement of the superficial resistance, also known as sheet resistance. If each couple of electrodes are placed in the top and bottom of the thin film respectively, the bulk resistance can be measured using the same configuration. Also, some interesting effects can be observed when the entire material takes part, and not only the superficial part.

The chemical nature of the electrodes and how they interact with the material are crucial variables in electric measurements. Different kinds of electrodes (Gold, Silver, and graphite) were used in the samples. The gold electrode is the commonest for industrial application, due to its long durability and excellent performance. Silver contacts are uncommon in de-
vices due to the easy oxidation with the environment, but its better conductivity could give more information for research proposes. Also, graphite is the cheapest option but has a considerable conductivity that can allow the operation of the device at a lower price.

Ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometry is a photon emission spectroscopic technique that uses electromagnetic radiation of a very precise wavelength, said radiation is absorbed, reflected, or transmitted by the sample, causing transitions that are quantified by the detector. To quantify the physical phenomena mentioned above, three optical parameters are used: spectral transmission (T), spectral reflectance (R), and absorbance (A). The UV-Vis-NIR spectroscopy employs a wide range of optical radiation, to carry it out is necessary three different lamps: a mercury lamp, a tungsten lamp, and a deuterium lamp, to be capable of covering a wide range of wavelengths from the electromagnetic spectrum (usually from 300 to 2500 nm). The measurement is done illuminating the sample under study with monochromatic electromagnetic radiation at a 90° angle and collecting information of the transmitted or reflected radiation after it has interacted with the sample.

For the magnetic characterization of the ZnO thin films, a magnetic properties measurements system (MPMS) based on the Vibrant Sample Method was used. The external magnetic field is generated with a superconducting coil, usually Ti/Nb, which allows it to achieve a high magnetic field variation with relative precision. In the vibrating sample method, the sample is subjected to sinusoidal motion between two pickup coils. The electrical output signal of these coils depends on the induced magnetic field and results with the same oscillation frequency of the sample and with an intensity proportional to the magnetic moments of the sample [261].

Since the magnetic moments fulfill the superposition principle, it is possible to substrain the contribution of the substrate. Assuming an isotropic distribution in each part, the magnetic behavior can be analyzed separately. First, the diamagnetic behavior can be subtracted by a simple calculation of its diamagnetic constant (χ):

\[ M_{m}^{tf}[H] = M_{m}^{sample}[H] - \chi HV^{dia}, \]  

(5-1)

where \( M_{m}^{tf(sample)} \) is the total magnetic moment of the thin film(sample), \( H \) is the external magnetic field and \( V^{dia} \) is the volume of the diamagnetic contribution. For example, for the samples over glass, \( \chi = -5,426(8) \) Oe emu\(^{-1}\)cm\(^{-3}\) and \( V^{dia} = width \cdot area_{sample} \) (\( width = 1,12(1) \) mm). This procedure is used to guarantee the isotropic of the magnetization, and separate the contribution of the sample from the substrate. In this way, a volume-normalization can be done and obtain the magnetization of the sample.
5.3. Methods and model

Electrical Current Vs. Voltage (I-V) characterization was performed by a Wenner method. A source-meter 2460 High-Current Interactive SourceMeter Instrument from Keithley was used in the 4-Wires configuration. The instrument has an accuracy of $\pm 10^{-12}$ A and $\pm 10^{-12}$ V, as source and meter. Electric measurements were made at room temperature and atmospheric pressure. Several cycles were made for I-V measurements, in Figures, only are showed one of each 50.

For the DC electric measurements in bulk, the samples were synthesized on the down electrodes (Fig. 5-1). The top electrodes were placed mechanically (Au) or by painting methods (Ag and graphite). The gold contacts always have a constant area of $0.094(8) \text{ mm}^2$ and the painted contacts have a bigger contact area of $\sim 0.74(6) \text{ mm}^2$. The distance between electrodes was fixed at $5.68(5) \text{ mm}$.

Magnetic properties of the samples were obtained through a commercial Quantum De-

Figure 5-1.: Arrangement of the different upper electrodes in the Co : ZnO film deposited on the lower electrode (ITO). On the right side, the configuration for sheet measurements can be observed.

sign magnetometer. This vibrating sample magnetometer has coupled a SQUID sensor and is capable of producing magnetic fields up to 30 kOe using a Ti – Nb superconductor coil. Measurements can be made within a temperature range between 50 K and 400 K, with an accuracy of 0.01 K. The equipment has a precision of $5 \times 10^{-9}$ emu. The magnetic characterization was performed by Magnetization as a function of the applied magnetic field ($M$ Vs. $H$) or the temperature. ($M$ Vs. $T$). The external magnetic field fixed in 300 Oe for the $M$ Vs. $T$ measurements. $M$ Vs. $H$ behavior was studied at 50 K, 150 K and, 300 K. The VSM works at a pressure of $\sim 2.5 \text{ kPa}$. Magnetization values were founded by a volume-normalization of the magnetic moments, the thickness and area of the thin films were directly measured by profilometer and optical microscopy respectively.
5 Electrical, optical and magnetic characterization of Cobalt doped ZnO thin films

The optical properties of the samples were obtained using a UV-VIS-NIR spectrophotometer reference T70 + UV/VIS from PG instruments at atmospheric pressure and room temperature.

Assisted laser impedance measurements (ALIS) measurement was performed in the same condition as the performed with DC with a Keysight E4980AL-precision LCR meter. All measurements were achieved with an AC signal of 1 V amplitude over a frequency range from 20 Hz to 1 MHz and with zero DC bias. Each point measurement was an average of 20 trials. Measurements were carried out at room temperature in a dark and electromagnetic isolated room. Before all ALIS experiments, a compensation protocol was performed, first with an open-loop configuration and then with a short-circuit connection, to correct for thermal noise and wiring, capacitance, and impedance leakage signals. Photonic excitation was realized with unpolarized TEM 00 solid-state lasers of wavelength $\lambda = 632$ nm (power of 149(1) mW mm$^{-2}$) and $\lambda = 390$ nm (power of 2.89(3) W mm$^{-2}$). All optics were assembled on a vibration-isolated breadboard. The compatible elements were acquired from Thorlabs. Moreover, to avoid parasitic signals, all ALIS facility is attached to an independent ground pole. The impedance noise for darkness or illumination is in the order of $\sim 9\Omega$, which is low in comparison to the smallest impedance [262].

All the fitting were performed using the least-squares method with a Levenberg Marquardt algorithm. Also, Magnetization curves were smoothed by an FFT with an 8-point window.

5.4. Results and discussions

As it was discussed above, some oxides have a resistive switching property when a voltage bias is applied through them. This determines the applicability in NVM technologies, then the different results obtained are shown based on the information of the current-voltage measurements and the different resistance variations. The theoretical condition to have this phenomenon is simple. An insulator (or semiconductor) between two conductive materials. For this reason, the samples studied were deposited over some conductor substrate (ITO, Gold, Ti, and Al). Also, different kinds of the top electrode were used (Graphite, Au, and Ag).

As it was expected, the thin films deposited by DC-Magnetron Sputtering of ZnO present a switching in the resistance. Fig. 5-2 shows a bipolar resistive switching behavior, a typical hysteresis of the RRAM. In these kinds of measurements the current has to be limited, cause in another case, the switching is permanent. If the current limit is too low, there are no changes in the resistance, or the resistance difference is too tiny. To have two well distin-
guish states is necessary to have a High Resistance State (HRS) and a Low Resistance State (LRS).

Figure 5-2.: Bipolar resistive switching for a sample of Au/ZnO/ITO thin film prepared at 423(2) K (250 cycles performed).

Also, in Fig. 5-2 can be observed that the first switching is energetically more expensive, and the consequent cycles have a dispersion around a central value. The central value of voltage in which the resistance change abruptly is known as the SET value or RESET value. The values of SET, RESET, first switching, optimal current limit, and resistance dispersion depend strongly on the synthesis parameters.

So, once the typical I-V curves are well obtained with ZnO as an insulator, it is time to add some Co impurities and see the effect in the phenomenon. The first thing that we observe
when the Co increases the resistance of the metal-insulator-metal (MIM) structure increase. For this reason, the current limit must be lower to avoid a short circuit. Fig. 5-3(right) shows the SET section of the I-V cycles for samples with different Cobalt target power. In these measurements, the limit current was fixed to 0.2 mA and the voltage bias was varied between -6 V and 6 V. Here the aperture of the curve is different for each Co concentration, and is too low for the undoped ZnO (black). The SET value at this limit current is very low for the sample with 8, 70 % (red) of Cobalt and the pure ZnO.

![Graph showing the relationship between Current and Resistance for different Cobalt concentrations.](image)

Figure 5-3.: Current (right) and resistance (left) in the switching cycles for Co-doped ZnO thin films at different $P_{Co}$ and prepared at 423(2) K. Current limit fix to 0.2 mA in all the 250 cycles.

Fig. 5-3(left) shows the resistance values for the same thin films as the right part. Here, the HR and LR states can be easily identified for the sample with Co at 14, 39 % (blue). A lot of dispersion is observed in the sample with 13, 19 % of Cobalt and it is difficult to distinguish the two resistance states. At this limit current, the lower concentrations of Co seems impossible to work as NVM.

Now, this limit current does not work well for every Cobalt concentration. So, a variation of this parameter was done from $5 \times 10^{-3}$ mA to 100 mA in each sample and the maximum hysteresis areas were saved. Fig. 5-4 shows the I-V cycles for the best current limit when the free parameter is the Cobalt concentration. In this case, all the samples have well-separated resistance states but once again is the thin film with the highest Co concentration the optimal NVM candidate.
5.4 Results and discussions

Figure 5-4: Current-Voltage SET cycles (250) for the different Co concentrations at their optimal (op) limit current.

The application and reliability of the device need to have into account the electrical power that is necessary for the set-reset process. Table 5-1 shows the average necessary powers to set and reset the memory cell. In an electronic device, no I-V curve is performed, quite the opposite, a pulse of fixed power is used to configure the bit and a lower pulse is used to read the value. This process is faster than the I-V measurement, and the time required to set or reset the value is known as the frequency of the memory. The values in Table 5-1 were calculated as the average area of the cycles in the set and the reset of the memory cell. The first values are for the optimal limit current and the last ones for \( I_{\text{max}} = 0.2 \) mA. A decrease in the power is found when the Cobalt concentration increases, due to the lower optimal current, that comes from the higher resistance at higher impurities concentration.

Another important parameter in the commutation MIM system is the thickness of the insulator. In Fig. 5-5 a comparison between the resistance states at optimal (op) limit current and fix it at 0.1 mA. Here can be observed the previous argument, a fixed current limit is not the best option for all the samples, that limit should change with every sample. The basic idea of a reliable NVM device starts with a resistance states such that their dispersion is much lower than their resistance gap. The fixed limit current meets this necessity only
5 Electrical, optical and magnetic characterization of Cobalt doped ZnO thin films

Table 5-1.: Powers of SET and RESET for different Cobalt concentration and current limit.

<table>
<thead>
<tr>
<th>$P_{Co}$</th>
<th>Co/Zn</th>
<th>$I_{max}$</th>
<th>Area SET</th>
<th>Area RESET</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>% at.</td>
<td>mA</td>
<td>mW</td>
<td>mW</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>50</td>
<td>18, 20(1, 43)</td>
<td>14, 17(2, 40)</td>
</tr>
<tr>
<td>20</td>
<td>8, 7</td>
<td>40</td>
<td>11, 35(82)</td>
<td>10, 59(89)</td>
</tr>
<tr>
<td>40</td>
<td>13, 19</td>
<td>0, 15</td>
<td>0, 203(33)</td>
<td>0, 105(22)</td>
</tr>
<tr>
<td>60</td>
<td>14, 39</td>
<td>0, 2</td>
<td>0, 549(29)</td>
<td>0, 014(9)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0, 2</td>
<td>0, 0025(1)</td>
<td>0, 0005(1)</td>
</tr>
<tr>
<td>20</td>
<td>8, 7</td>
<td>0, 2</td>
<td>0, 015(2)</td>
<td>0, 025(1)</td>
</tr>
<tr>
<td>40</td>
<td>13, 19</td>
<td>0, 2</td>
<td>0, 198(29)</td>
<td>0, 015(13)</td>
</tr>
<tr>
<td>60</td>
<td>14, 39</td>
<td>0, 2</td>
<td>0, 550(29)</td>
<td>0, 014(9)</td>
</tr>
</tbody>
</table>

once in a while. So, make sense to study the other requirements only with the optimal limit current. The optimal thickness for the electrical properties, the highest resistance gap with the lowest dispersion, was $\sim 130$ nm ($t_d = 15$ min).

Figure 5-5.: Average LRS and HRS as function of the deposit time for Co-doped ZnO at 13, 19 %. The limit current was the optimal (red and black) or fix at 0, 1 mA (blue and red). Error bars represent the state dispersion of the average over 250 cycles.
Now, it is possible that the dispersion increase with the re-writing of the memory. Mostly commercial memories guarantee at least 10 000 cycles until 100 000. This can be studied from the increasing of the dispersion with the cycles, and extrapolate until the dispersion reach a considerable fraction of the gap.

Fig. 5-6 shows the low and high resistance states as a function of the number of cycles. The state was set and reset by fixed power pulses according to the Table 5-1 and measured at 1 V after the bit was written. The behavior oscillates around central values, and the dispersion is around 1.5 MΩ in both cases. Due to the higher resistance gap, the device is still reliable, and no deformation is observed after the 16000 set and reset processes.

Figure 5-6.: Low and high resistance states as a function of the number of cycles for a Au/Co : ZnO/ITO system.

Once the device has two well-distinguish resistance states, the next important requirement for an NVM is its non-volatile condition. For this test, the memory cell was set it up in the
LRS, and some measurements along the time were performed. Fig. 5-7 shows the behavior of the LRS as a function of the time for $10^5$ seconds. Green triangles show the measurements and the dash-line shows the average HRS measured before the set, and after the reset of the commutation system. The fluctuations in the time are lower than the fluctuation in the cycles, which gives a lot of confidence in the save of the information, even extrapolating to the 20 years of the set, the resistance state still in the accepted range.

![Graph showing LRS and average HRS as a function of time](image)

Figure 5-7.: LRS and average HRS as a function of the time for a Au/Co : ZnO/ITO system.

The device can be affected by an external source of light and change its resistivity states. For this reason, it is important to check if there is some energy for which the photons are absorbed by the material. Fig. 5-8 shows the absorbance spectrums as a function of the Cobalt concentration, an increase in the absorbance is observed with the Co, as expected [263]. Also, comparing the pure ZnO with the doped samples appears some slight peaks in the spectrum. These peaks are marked in the figure and correspond to optical excitations of the d-d bond of the Cobalt [264]. This bond is a particularity of the Co oxidation state $+2$, that could confirm a substitutional impurity into the ZnO matrix.
Figure 5-8.: Absorbance spectrum for different Cobalt concentrations in $Co:ZnO/Glass$.

From the absorbance spectrums, using the Beer-Lambert law [265] the band-gap could be calculated. Table 5-2 shows the values of the forbidden band for the samples over Glass, and over ITO. A UV-shift is observed when the Cobalt increases in the structure. The fact that the shift never collapses is a good clue of the no formation of secondary phases [252].

Table 5-2.: Gap values for the different $Co$ concentrations in the $ZnO$ thin films over glass and ITO.

<table>
<thead>
<tr>
<th>$P_{Co}$ W % at</th>
<th>Co/Zn</th>
<th>Gap-Glass eV</th>
<th>Gap-ITO eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>3.19(6)</td>
<td>3.26(3)</td>
</tr>
<tr>
<td>20</td>
<td>8.7</td>
<td>3.26(3)</td>
<td>3.31(14)</td>
</tr>
<tr>
<td>40</td>
<td>13.19</td>
<td>3.28(1)</td>
<td>3.29(2)</td>
</tr>
<tr>
<td>60</td>
<td>14.39</td>
<td>3.45(1)</td>
<td>3.29(4)</td>
</tr>
</tbody>
</table>

Now there is a particular interest in a model to explain the behavior inside the bulk in the high resistance state. It is well known that the low resistance state behaves like an ohmic material. But the reason why the resistance switching and how it can be modeled...
remains a question. To have a first approach to solve these questions was studied the electrical response of the material through an AC electromagnetic field. The amplitude of the complex impedance of the bulk and the phase change in the resultant signal was measured as a function of the signal frequency. Fig. 5-9 shows the impedance amplitude and phase for four different concentrations of Cobalt (Bode plot). The bulk impedance increase with the impurity concentration, in amplitude and phase. The amplitude behavior has the same start and in the high-frequency zone are subsequent endings.

![Bode plots for the impedance bulk measurement of Au/Co : ZnO/ITO systems at different Cobalt concentrations: 0 % at. (a), 8.7 % at. (b), 13.19 % at. (c), and 14.39 % at. (d).](image)

Figure 5-9.: Bode plots for the impedance bulk measurement of Au/Co : ZnO/ITO systems at different Cobalt concentrations: 0 % at. (a), 8.7 % at. (b), 13.19 % at. (c), and 14.39 % at. (d).

That can be observed better in a normalized Nyquist plot (Fig. 5-10), here all the Z values are normalized by the maximum value of the real part (Z₀). Here can be observed how each curve appears to be completed by the next concentration, starting as a sim-
5.4 Results and discussions

ple Capacitor-resistance \[266\] for the undoped material, and become showing a resistance-
capacitor//resistance typical behavior when the Cobalt concentration increases \[267,268\].

Figure 5-10.: Normalized Nyquist plot for different Cobalt concentrations in the Co : ZnO/ITO thin films. The inset shows the low frequencies range for the highest concentration of Cobalt.

For the doped samples, Table 5-3 shows the values of the equivalent circuit for each case. The electrical model was chosen as a resistance in series with parallel resistance and capacitor, the series resistance represents the facility of the electric wire in the switching most accepted model, and the parallel circuit represents the accumulated ions in each electrode as a real capacitor. The series resistor increase with the magnetic doping agreeing with the previous electric measurements, while the capacitor remains almost constant, appearing to be an effect of the contacts, the second resistor increases dramatically with the Cobalt concentrations, resulting in a response to higher frequencies. Previously, the optical absorption and consequently the gap of the thin films were determined as a function of the magnetic doping, using these results, two optical stimuli could give information of the samples, the UV/Violet and the red. The first one should affect the whole thin film, with a bigger proportion at higher gaps, and in a proportional way to the ZnO quantity in the sample. Fig. 5-11 (left) shows the impedance amplitude reduction (better conductivity) and the phase shift \((\theta_{UV} - \theta_{dark})\) as a function of the frequency. The phase shift increases at high frequencies and has a peak for the higher impurity concentration, appearing that once again is the same behavior in all samples, with just a shift in the frequencies. On the other hand, the red
stimulus only has an evident effect in the highest Co concentration (Fig. 5-11(right)). The other samples present a slight improvement in their conductivity, but no correlation with the magnetic concentration was founded. The thin film prepared at 60 W of Cobalt power, present some erratic peaks in the amplitude reduction, suggesting that probably different bonds are present in the material.

The sheet resistivity was studied to determine the superficial electric mobility in the material as a function of the Cobalt concentration. Like the bulk resistivity, the sheet resistivity increase in several magnitude orders with the magnetic impurities, showing a phase transition from a pure semiconductor to an insulating alloy. Finally, the effect of the top contact was measured in term of the necessary power to set[reset] the resistance state in the material, at 0.15 mA as the limit current, the power values (mW) decrease significantly from 0.203(33)[0.105(22)] for the Au contact to 0.016(3)[0.005(3)] and 0.015(2)[0.043(12)] for Ag and graphite top contact respectively. This could be very good to have an efficient material for an electronic application.
5.4 Results and discussions

Figure 5-12: Sheet resistivity of $Co:ZnO$ for different Cobalt concentrations in the 0-6 V range.

To finish the experimental results, the magnetic properties of the $Co$-doped $ZnO$ thin films were studied. Here, the goal is to achieve a relevant magnetic behavior at room temperature, full-filling the DMS conditions. In the experimental details of the thin-films synthesis, was mentioned that posterior annealing to the deposit is a requirement to have remarkable magnetic properties. Fig. 5-13a shows a comparing in the magnetization when the sample is annealed at 473(2) K. The effect of the annealing is evident, at low temperatures when the annealed sample has a strong competition between a ferromagnetic interaction and a diamagnetic contribution. Also, at 150 K the magnetization values are lower for the annealed sample. Fig. 5-13b shows a zoom where is observed a slight hysteresis at 150 K with a tiny remainder magnetization and a considerable coercive field.
68 Electrical, optical and magnetic characterization of Cobalt doped ZnO thin films

Figure 5-13.: Annealing effect in the magnetization as a function of the externally applied field. Measurements realized at 150 K (a, c) and 300 K (b) of Co-doped ZnO/Glass at 13, 19 %. Sub-figure c shows zoom-in low fields.

However, at room temperature (Fig. 5-13b) no hysteresis was observed. Trying to achieve this goal, the previous results were analyzed. From the theoretical study, the Cobalt substitution in the wurtzite structure results in an efficient DMS. Also, the XRD results show that the amorphous soda-lime glass maybe is not the best substrate to introduce the doping. So, remember that the samples deposited on Al₂O₃ substrate were the most crystalline, is a good idea to study the magnetic properties on these thin films. Nevertheless, the 100% diamagnetic contribution of the glass is easy to take off, and there is some uncertainty about how to have only into account the contribution of the thin films synthesized over Al₂O₃.

Fig. 5-14 shows the magnetization of the Al₂O₃ substrate as function of the magnetic field. Also, it shows the magnetization without diamagnetic contributions. The diamagnetic constant was calculated assuming a linear combination of several magnetization sources. As the behavior is almost diamagnetic in high fields, the slope of the M-H curve was calculated by a linear fit. $\chi = -4.58(3) \times 10^{-5}$ emu cm$^{-3}$ Oe$^{-1}$ was the diamagnetic constant found for Al₂O₃. Following the same procedure as the glass's contribution, the diamagnetic contri-
bution of \( Al_2O_3 \) was subtracted from all the subsequent H-M measurements (\( \chi = -4.59(3) \) emu Oe\(^{-1}\)cm\(^{-3}\)).

![Magnetization of the \( Al_2O_3 \) substrate as function of the magnetic field](image)

**Figure 5-14:** Magnetization of the \( Al_2O_3 \) substrate as function of the magnetic field (red line) and No-diamagnetic magnetization contribution (black line). The inset shows these magnetization at low external fields.

The inset in Fig. **5-14** shows a weird hysteresis in the original measurement of the substrate, however, it disappears when the diamagnetic contribution is subtracted. Now, without the diamagnetic contribution of the substrate, the interest is the focus on the magnetization effect of the Cobalt concentration. Remembering that Co ions increase his presence in the semiconductor matrix at highest \( P_{Co} \) (\( P_0 = 0\) at., \( P_{20} = 8,70\) at., \( P_{40} = 13,19\) at., and \( P_{60} = 14,39\) at.). Fig. **5-15** shows comparative M-H curves for each different \( P_{Co} \), those powers corresponds to relative Cobalt concentration according to Auger measurements.
Figure 5-15.: M-H curves for each different $P_{Co}$ at 300 K. Blue(black) lines correspond to the blue(black) magnetization scale.

The two highest concentrations have significantly higher magnetization (blue scale). The pure ZnO seems like a paramagnetic that saturates very fast. A tiny hysteresis is observed in the thin film with Co at 8.70% ($P_{20}$) and like the $Al_2O_3$ substrate, the $P_{40}$ exhibits a disoriented hysteresis. The change in the shape of this magnetization is evident, cause a strong diamagnetic contribution appears ($\chi = 5.66(2) \times 10^{-3}$ emu cm$^{-3}$ Oe$^{-1}$). The hysteresis here has a remainder magnetization of 1.92(2) emu cm$^{-3}$ and a coercive field of 1,31(17) KOe. With the highest Co concentration, the interaction between Co defeats the diamagnetic contributions and shows a long and thin hysteresis. However, is not visible at this scale. Fig 5-16b shows a scope at low fields of the hysteresis. It has a lower remainder magnetization (0.9(3) emu cm$^{-3}$) and coercive field (450(30) Oe). When the temperature down (Fig 5-16a) the hysteresis loop still thin, but is more defined and has a larger coercive field. Fig. 5-16 shows the FC M-T curve at 300 Oe of this sample. From the FC curve can be concluded that for this sample, the temperature is not an order parameter at least in the 50K-300K range.
Figure 5-16: Magnetization as a function of the external field at 50 K (a) and 300 K (b), for the Co:ZnO thin film doped at 14.39%. (c) FC curve at 300 Oe for the same sample.
6. Conclusions and perspectives

6.1. Conclusions

ZnO and Cobalt doped ZnO thin films were successfully fabricated by DC-magnetron co-sputtering method. For this purpose, there were used Cobalt and Zinc oxide targets in a non-reactive sputtering machine with Argon as plasma gas. Several samples were prepared with different synthesis parameters (Cobalt power, deposit time, substrate temperature, chemical nature of substrate), with a thickness of the thin films between 50 and 190 nm, and optically transparent.

Based on \textit{ab-initio} calculations and mean-field Heisenberg model, the effect of the $V_O$ in Co-doped ZnO is principally an electron spin density redistribution around the $V_O$, which depends strongly on the $Co-V_O$ distance and the ratio of concentrations $Co : V_O$. All different $V_O$-configurations presented a lower total magnetization (per $Co$ atom) than their equivalents without vacancies. But the increase of $Co-V_O$ distance reduces the local magnetic moment on the $Co$ atom, which is due to the antiferromagnetic coupling between $Co$ and $V_O$ impurity for the lowest distances $Co-V_O$. Formation energy shows an increment when the $Co$ concentration and the $Co-V_O$ distance raised but the average magnetization per Cobalt seems to not correlate with the $Co$ concentration. However, a different effect was observed a second oxygen vacancy was added close to the first one. In the 1 : 2 ratio case, we found a maximum effect radius $\Delta_2 \leq 3.5\,\text{Å}$. When the second $V_O$ was closer than that, the electron spin distribution around Cobalt impurity was concentration depended, increasing or decreasing the magnetization ($TMM/Co$). In all configurations, magnetic moments were mainly generated by $Co - 3d$ orbitals and the presence of $V_O$ helped to the ferromagnetic stabilization with high Curie temperatures when the $Co-Co$ distance was lowest. Charge spin distribution allowed to note that the $V_O$ presence increases the antiferromagnetic electronic spatially distributed. This explains the $TMM/Co$ decrease by the $V_O$ helped the ferromagnetic interaction between Cobalt atoms, working as an exchange bridge.

The Cobalt distribution as a function of the target power allowed the selection of the optimal samples for the DMS condition of no secondary phases in the semiconductor matrix. Also, a logarithmic tendency was found in the thickness of the samples as a function of the deposit time and an increase of it with the Cobalt concentration was evidenced. Through Auger spectroscopy, a random distribution of the Cobalt into the bulk was found, and quan-
tification of the atoms was performed. The Cobalt concentrations, relative to the Zinc in the studied samples, was on average 8.70 %, 13.18 %, and 14.38 % for the powers of $P_{Co} = 20\text{W}, 40\text{W}, 60\text{W}$ respectively. In the diluted matrix, was found a 0.49 ratio for the $O:Zn$ atoms, implying several oxygen vacancies in the structure, the possibility of Zn clusters was denied by XRD measurements and the high electrical resistance.

Structural characterization revealed the typical wurtzite phase of ZnO and growth in the substrate preferential planes. Secondary phases of Co were not found by XRD measurements. However, a decreasing shift in the position of the peaks was evidenced when the Co concentration increases. No relevant change in the diffraction patterns was observed when the substrate temperature increased, probably due to the fact of the in situ annealing of a higher temperature. Same reason for the no relevant changes in the topography of the thin films deposited at different temperatures.

A correlation between the chemical nature of the substrate and the topography was observed in the micrographs by SEM. To study the morphological effects of the Cobalt concentration, AFM measurements were performed. Here, a Co tip was used to additionally study the magnetical response of the surface. The grain size increased in the function of Cobalt and some remarkable magnetic grains were identified in the highest concentrations. For the 15% Cobalt sample, a magnetic distribution in the surface was observed, where the upper RMS/M-RMS was present.

The resistive switching phenomenon was observed in the pure ZnO and $Co:ZnO$ thin films. The higher electric power of the first set is in agreement with the proposed models for the effect. It showed a strong dependence with the current limit of the set-reset process and each sample exhibited an optimal current limit, i.e. the current in which the high and low resistance states are more separated and less dispersed. The resistive gap between the LRS and the HRS is enough to propose a memory application, which increases with the resistance values and the Co concentration. Also, the required electrical power to set or reset the bit in the memory was lower when the magnetic impurities increases.

The optimal deposit time for the memory application was 15 minutes, where the relation between the HRS-LRS separation and the dispersion of the measurement was the best. The reliability of the device was tested with 16000 cycles and dispersion of $\sim 3 \text{ M}\Omega$ in each resistive state was found. The separation of the states is enough to take this dispersion without jeopardizing the reliability. Also, the condition of non-volatile was tested, performing measurements for $10^8$ seconds with only one set pulse. The time-behavior of the set state was steady and it guarantees the duration of the data for a long time (can be extrapolated until the standard 10 years from the market).
Optical characterization shows an increase in the opacity of the thin films with the Cobalt concentration and exhibited some absorption peaks associated with Co d-d bonds in the structure. Through the Beer law, the energy forbidden band was calculated as a function of the impurities concentration. It had a UV-shift that increases with the absorption.

Also, magnetic characterization of the samples showed hysteresis loops in the magnetization at room temperature. The crystallinity of the samples played an essential role in the magnetic behavior, represented by the annealing requirement and the substrate dependence. The magnetization hysteresis had a remainder magnetization of 1.9(2) emu cm$^{-3}$ and a coercive field of 1.31(17) KOe for the sample with 13.19% of Cobalt. From the FC curve can be concluded that for this sample, the temperature is not an order parameter at least in the 50 K-300 K range.

Finally, due to the coexistence between the magnetic and the electric properties of the Co-doped ZnO, several spintronic applications can be performed using these thin films as precursors. Using resistive switching and remanent magnetization, a higher-density memory cell can be formulated with a layer of the undoped material between two films of the doped one, as Andrew W. Stephan et. al. proposed theoretically [269]. Also, with the properties showed it is possible to formulate spin-valves [270] or spin-polarized transistors, that have serious troubles with the Curie temperature of the current spintronics [271].

### 6.2. Perspectives

Due to the fact that the $Co : ZnO$ is a well-studied material, the principal perspectives of this work are about the applications. However, the industrial closeness of the sputtering technique, makes it deserve a deeper analysis into the growth and crystalline structure formation. Also, the explanation of the ferromagnetic behavior in this material remains an open question.

The possible magnetoresistance effect in this material could bring it close to a spintronic application, also probably the magnetic impurities under external magnetic fields could increase the frequency of the device, as in the case of Giant magnetoresistive nanopillars and the Spin-orbit torque devices.

The wide band-gap of the material and the well-known electrical properties of the pure semiconductor could have an interesting application in optoelectronic science and technology. A possible spin-valve at room temperature could be the best simple spintronic device of $Co : ZnO$.

Also, continue as doubt the presence of possible segregated Cobalt phases in the samples,
which should be cleared by other characterization techniques as XPS.

6.3. Peer-reviewed articles

Among the production of this work, some articles in peer-reviewed journals were published or are in the peer review process.

6.3.1. ZnO DFT approach

- (In peer review process) Physica Status Solidi (b) Influence of Oxygen vacancies on Room-temperature ferromagnetism in Cobalt-doped ZnO. F. Galindez, Rafael González-Hernández, A. Dussan, and Victor Mendoza

6.3.2. Cobalt influence in DMS


A. Appendix: Purity report of ZnO and Co targets

![Certificate of Analysis Image]

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Note: Typical Analysis of Starting Material Only

Date of Certification: 06/30/2014

By: __________________________
# Certificate of Analysis

**Customer Name:** Vortex Company  
**Material:** Zinc Oxide  
**Purchase Order No.:** 1099  
**Composition:** ZnO  
**Lot Number:** PLA49080390  
**Size:** 3" Dia X 0.125" Thick  
**Product Description:** Sputtering Target  
**Purity:** 99.99%

## Spectrographic Analysis

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Note: Typical Analysis of Starting Material Only

**Date of Certification:** 12/30/2015  
**By:**

2268 Research Drive, Livermore, CA 94550
B. Appendix: Substrates data-sheet

REMISSION

ITO Coated Corning Glass for R&D Use
Indium Tin Oxid (ITO) coated onto corning glass. DepotNano
Low sheet resistance and high transmittance,
Applications: OLED, OPV, electrochromic devices, electrochemistry, Low-Temperature Solution-Processed Perovskite Solar Cells.

Parameters:
Substrate: corning
Sheet resistance: <10 ohm/sq
Transparency: >83%
Roughness: < 3 nm
Thickness of conductive layer =180.0 ± 15.0 Å
Working temperature: up to 300 °C
Certificate of Analysis

Product Name: Silicon, wafer (single side polished), <100>, N-type, contains phosphorus as dopant, diam. × thickness 3 in. × 0.5 mm

Product Number: 647802
Product Brand: ALDRICH
CAS Number: 7440-21-3
Molecular Formula: Si
Molecular Weight: 28.09

TEST

SPECIFICATION
LOT 10725KC RESULTS
GREY DISC
(100) DOPED N-TYPE 3"DIAM
SEPTEMBER 2004

Barbara Roger, Supervisor
Quality Control
Milwaukee, Wisconsin USA
C. Appendix: PDF files from XRD analysis

Date: 1/02/2021 Time: 6:54:04 p.m. 
File: A1203 
User: Alejandra

**Name and formula**

Reference code: 00-004-0787
Mineral name: Aluminum, syn
Compound name: Aluminum
PDF index name: Aluminum
Empirical formula: Al
Chemical formula: Al

**Crystallographic parameters**

Crystal system: Cubic
Space group: Fm-3m
Space group number: 225

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\[ c (\text{Å}): 4.0494 \]
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\[ \text{Beta (°)}: 90.0000 \]
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Volume of cell (Å\(^3\)): 66.40
\[ Z: 4 \]
\[ \text{RIR}: 3.62 \]

**Subfiles and quality**

Subfiles: Alloy, metal or intermetallic
Common: Phase
Educational: pattern
Explosive
Forensic
Inorganic
Mineral
NBS pattern
Pigment/Dye

Quality:

**Comments**

Color:

Creation Date: 1/01/1970
Modification Date: 1/01/1970

Color:

Sample Preparation: The material used for the NBS sample was a melting point standard sample of aluminum prepared at NBS, Gaithersburg, Maryland, USA

Analysis: The chemical analysis (%): Si 0.0011, Cu 0.006, Fe 0.007, Ti 0.0001, Zr 0.003, Ga 0.004, Mo 0.00002, S 0.0001, Al 99.9+ (by difference). Temperature of Data Collection: Pattern taken at 25 C. Mineral species of doubtful validity, *Am. Mineral.*, 65 205 (1980). Additional Patterns: See ICSD 64700 (PDF 85-1327).
C Appendix: PDF files from XRD analysis

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**Comments**

Creation Date: 1/01/1970
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<td>4.7040</td>
</tr>
<tr>
<td>b (Å):</td>
<td>4.7040</td>
</tr>
<tr>
<td>c (Å):</td>
<td>5.2610</td>
</tr>
<tr>
<td>Alpha (°):</td>
<td>90.0000</td>
</tr>
<tr>
<td>Beta (°):</td>
<td>90.0000</td>
</tr>
<tr>
<td>Gamma (°):</td>
<td>120.0000</td>
</tr>
<tr>
<td>Calculated density (g/cm$^3$):</td>
<td>2.97</td>
</tr>
<tr>
<td>Volume of cell (Å$^3$):</td>
<td>1008.82</td>
</tr>
<tr>
<td>Z:</td>
<td>3</td>
</tr>
<tr>
<td>RIR:</td>
<td>2.70</td>
</tr>
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</table>

### Status, subfiles and quality

<table>
<thead>
<tr>
<th>Status:</th>
<th>Diffraction data collected at non ambient pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subfiles:</td>
<td>Alloy, metal or intermetallic Inorganic Modelled additional pattern Pharmaceutical</td>
</tr>
<tr>
<td>Quality:</td>
<td>Calculated (C)</td>
</tr>
</tbody>
</table>

### Comments

- ICSD collection code: 016335
- Creation Date: 1/01/1970
- Modification Date: 1/01/1970
- ICSD Collection Code: 016335
- ICSD SG: P3221

### References

- Primary reference: *Calculated from ICSD using POWD-12++, (1997)*
**Name and formula**

Reference code: 01-080-0074

Compound name: Zinc Oxide

ICSD name: Zinc Oxide

Empirical formula: OZn

Chemical formula: ZnO

**Crystallographic parameters**

Crystal system: Hexagonal

Space group: P63mc

Space group number: 186

a (Å): 3,2538

b (Å): 3,2536

c (Å): 5,2151

Alpha (°): 90,0000

Beta (°): 90,0000

Gamma (°): 120,0000

Calculated density (g/cm^3): 5,65

Volume of cell (10^-6 pm^3): 47,91

Z: 2,00

RIR: 5,44

**Subfiles and quality**

Subfiles: Alloy, metal or intermetallic

Corrosion

Inorganic

Modelled additional pattern

Pharmaceutical

Quality: Calculated (C)

**Comments**

ICSD collection code: 067848

Creation Date: 1/01/1970

Modification Date: 1/01/1970

ICSD Collection Code: 067848

Calculated Pattern Original Remarks: REM RVP

Calculated Pattern Original Remarks: REM K ZnO obtained from beta-Zn(OH)Cl

Temperature Factor: ITF

**References**

Primary reference: Calculated from ICSD using POWD-12++, (1997)

Bibliography


[89] Young Mok Cho, Woong Kil Choo, Hyojin Kim, Dojin Kim, and Youngeon Ihm. Effects of rapid thermal annealing on the ferromagnetic properties of sputtered Zn1-x(Co0.5Fe0.5)xO thin films. Applied Physics Letters, 80(18):3358–3360, may 2002.


[115] Argon (Ar) - Chemical properties, Health and Environmental effects.


[211] Principios básicos del microscopio electrónico de barrido.


