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STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF ZnO AND ZnO:CO NANOSTRUCTURES THIN FILMS FOR OPTOELECTRONIC APPLICATIONS

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ABSTRACT

This study comparatively evaluates the influence of Co incorporation on these properties in films deposited onto glass, titanium and Silicon substrates by DC magnetron co-sputtering. Structural, compositional, morphological, optical, and electrical characteristics were investigated using X-ray diffraction (XRD), Raman, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), Ultraviolet–Visible–Near-Infrared (UV–Vis–NIR) spectroscopy, current/voltage (I–V) measurements, cycling-endurance tests, and temperature dependent conductivity analysis. The hexagonal wurtzite structure was retained after Co incorporation, but diffraction-peak shifts are evidenced, vibrational-band modifications, and a rougher granular morphology indicated lattice perturbation and increased local disorder. XPS measurements support the presence of cobalt as a dilute dopant in the ZnO-based film. Also, the optical band gap narrowed from 3.16 eV to 2.70 eV and the estimated film thickness from 100.57 to 93.04 nm, using an iterative Bhattacharyya method. The ZnO:Co device exhibited a wider separation between the high and low resistance states (HRS/LRS) and bipolar resistive switching and a thermally activated transport, with SET and RESET transitions near -0.9 V and $+0.5$ V, respectively although progressively increase of resistive levels during the endurance tests. A thermally activated transport mechanism at high temperatures was shown, with an activation energy of 44.7 meV for ZnO and 242.91 meV for ZnO:Co. These results demonstrate that dilute Co incorporation simultaneously modifies the structural, optical, and electrical response of ZnO thin films, offering a promising pathway for the design of multifunctional optoelectronic devices.

Keywords: Co-doped ZnO; thin films; DC magnetron co-sputtering; resistive switching; optical band gap; X-ray photoelectron spectroscopy

1. Introduction

Zinc oxide (ZnO) has been established as one of the most versatile and promising semiconductors for technological applications. This compound exhibits a wide energy band gap of ~ 3.37 eV, stable electron-hole pairs, high photosensitivity, and optical transparency around 85% across a broad wavelength range extending from the ultraviolet to the visible region [1,2]. In addition, ZnO is not toxic and exhibits piezoelectric properties, as well as excellent chemical and thermal stability [3–5]. In the global context of energy transition and electronic device miniaturization, nanostructured ZnO thin films represent a low-cost and highly scalable alternative for the development of solar cells, ultraviolet photodetectors, and non-volatile resistive memories (RRAM) [6–8].

The incorporation of transition-metal dopants into oxide-based semiconductor matrices has become a highly effective strategy for tuning their structural, electrical, and optical properties according to the requirements of specific applications. Among the dopants most widely investigated for application in ZnO, cobalt (Co) have a prominent position due to the similarity between its ionic radius and that of zinc. In fact, the ionic radius of Co^{2+} (0.58 Å) closely matches that of Zn^{2+} (0.60 Å), differing by approximately 3%, which facilitates its substitutional incorporation into the hexagonal wurtzite lattice sites without inducing structural distortions or secondary phases, as confirmed by previous studies using X-ray diffraction (XRD) [9–11]. This structural compatibility induces changes in energy levels and surface states of the material, allowing band-gap engineering and the introduction of magnetic properties, consequently, ZnO:Co can be simultaneously employed in spintronic and optoelectronic devices within a single material platform.

Numerous investigations have documented the effects of cobalt doping on the physical properties of ZnO, however, few studies have comprehensively analyzed the impact on optical, electrical, magnetic, and structural properties simultaneously and comparatively across films fabricated under a single, consistent synthesis method. [11–13] Furthermore, several challenges also remain in the understanding of conduction mechanisms and their relationship with structural defects, the role of oxygen vacancies, and the optical behavior of ZnO:Co thin films [14–16]. In the field of resistive memories, ZnO has emerged as one of the most widely employed materials for RRAM devices, exploiting the reversible resistive switching mechanism between a high-resistance state and a low-resistance state, while offering benefits such as high storage density, low power consumption, operational stability, and long retention [7,8,17–19].

This work presents a comprehensive and comparative analysis of the structural, electrical, and optical properties of nanostructured ZnO and ZnO:Co thin films synthesized by DC magnetron sputtering onto glass and titanium (Ti) substrates, evaluating the impact of cobalt doping on each of these dimensions. The controlled incorporation of Co^{2+} into the ZnO crystal lattice is expected to modify the optical band gap, electrical conductivity, and surface morphology of the material, thereby extending its spectral absorption range and enhancing its resistive switching characteristics.

2. Materials and Methods

2.1. Synthesis of ZnO and ZnO:Co Thin Films

ZnO and ZnO:Co thin films were synthesized by DC magnetron sputtering onto glass substrates and titanium foils. The substrates were prepared by cleaning them with Alconox, distilled water, deionized water, and drying them with gaseous N_2 (99.95%). A ceramic ZnO target and a metallic Co target were used for deposition in an argon atmosphere. For the pure ZnO films, the deposition time was 20 minutes, with a power of 100 W applied to the ZnO target. In the case of the doped films (ZnO:Co), the deposition time remained constant at 20 minutes with 100 W applied to the ZnO target and 50 W to the Co target. Both films were deposited at a working pressure of 2.5×10^{-2} Torr.

2.2. Characterization Methods

The structural characterization of the films was carried out by X-ray diffraction (XRD), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). XRD measurements were performed at Universidad

Industrial de Santander (UIS) using a BRUKER D8 ADVANCE diffractometer with DaVinci geometry and CuK α 1 radiation. The diffractograms were collected in the 2 θ range from 10° to 90°, using an operating voltage of 40 kV, a current of 40 mA, and a step size of 0.01°. Raman spectra were acquired over the 100–500 cm^{-1} spectral range using a Horiba Xplora Plus Raman microscope equipped with a 532 nm excitation laser.

FTIR spectroscopy was used to identify the main vibrational modes associated with the chemical bonds present in the samples. The measurements were carried out using a JASCO FT/IR-4700 spectrometer in the infrared region, under atmospheric pressure and room-temperature conditions. FTIR spectra were analyzed in the 400–1000 cm^{-1} wavenumber range. The surface elemental composition and chemical states were investigated by X-ray photoelectron spectroscopy (XPS) at UIS using an XPS/ISS/UPS-ACenteno surface-characterization platform manufactured by SPECS GmbH (Germany). The system was equipped with a PHOIBOS 150 CMOS hemispherical electron-energy analyzer and a monochromated Al K α X-ray source (FOCUS 500) operated at 200 W. The analyzer pass energy was set to 100 eV for the survey spectra and 20 eV for the high-resolution spectra. Surface charging was compensated during acquisition, and the binding-energy scale was corrected by referencing the C–(C,H) component of the adventitious-carbon C 1s peak to 284.8 eV.

Surface morphology was analyzed by scanning electron microscopy (SEM) using a Tescan VEGA3 microscope. SEM images were acquired at different magnifications using secondary electron detection. The elemental composition was evaluated by energy-dispersive X-ray spectroscopy (EDX), and the results were reported in normalized weight percentage, wt.%, including the uncertainty provided by the equipment. The electrical response of the films was evaluated from current–voltage characteristics and temperature-dependent conductivity measurements using a Keithley 2460 source meter. Measurements were performed under atmospheric pressure and high-vacuum conditions about $\sim 8 \times 10^{-6}$ Torr. The vacuum system consisted of a mechanical pump coupled to a turbomolecular pump, and the pressure was monitored using a Pfeiffer PKR 251 cold-cathode gauge. Temperature control was achieved using a 10 Ω resistive heater powered by a GW Instek PSP-603 power supply. The temperature was measured with a type-K thermocouple and recorded using an NI 9219 data acquisition module connected to a cDAQ-9171 chassis. Additionally, the optical properties were studied using a T70+ UV-VIS-NIR spectrophotometer, capable of measuring absorbance, transmittance and reflectance in the 190–1100 nm.

3. Results

3.1. XRD

The structural properties of the undoped ZnO and ZnO:Co thin films deposited on titanium substrates were investigated by X-ray diffraction, as shown in Fig. 1. The diffractograms reveal the coexistence of weak ZnO-related reflections and intense diffraction peaks associated with the metallic Ti substrate. The dominance of the Ti reflections indicates that the diffracted signal is strongly influenced by the substrate contribution, which is expected for thin films when the penetration depth of the incident X-ray beam is comparable to or larger than the film thickness.

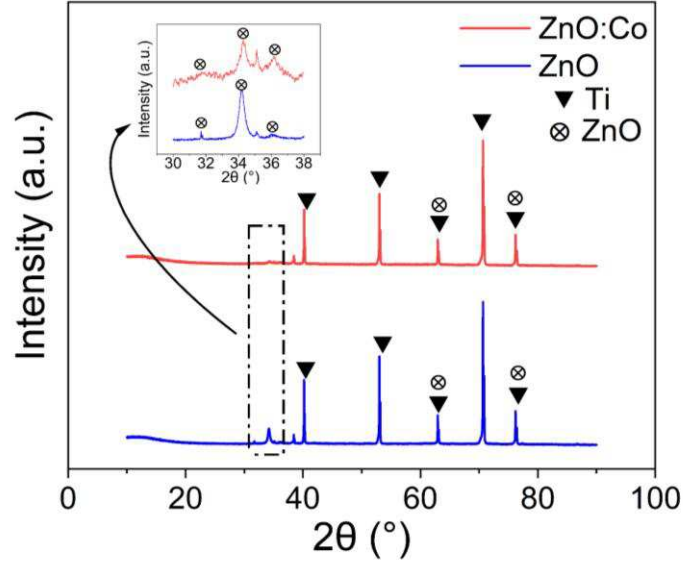


Figure 1. XRD patterns of ZnO and ZnO:Co thin films deposited on Ti substrates. The intense peaks marked with ▼ correspond to the titanium substrate, whereas the ZnO-related reflections, marked with ⊗, are assigned to the hexagonal wurtzite phase. The inset highlights the enlarged 30°–38° 2θ range, showing the shift of the ZnO diffraction peaks after Co incorporation.

Although the overall diffraction response of the films is broad and of relatively low intensity, weak but distinguishable reflections associated with the ZnO phase are observed in the enlarged region between 30° and 38° in 2θ with a R_{wpx} of 7%. For the undoped ZnO film, the peaks located at approximately 31.79°, 34.19°, and 36.09° are assigned to the (100), (002), and (101) planes of hexagonal wurtzite ZnO, respectively. These reflections indicate that the ZnO thin film preserves the characteristic wurtzite structure, even though its crystallinity is limited by the thin-film nature of the sample and the strong substrate contribution. Similar behavior has been reported in ZnO-based thin films, where the wurtzite phase is commonly retained despite variations in crystallinity associated with deposition conditions, film thickness, and dopant incorporation [15,20,21].

For the ZnO:Co thin film, the corresponding ZnO-related reflections are shifted to approximately 31.91°, 34.26°, and 36.14° for the (100), (002), and (101) planes, respectively. The preservation of these characteristic diffraction peaks suggests that the ZnO wurtzite framework is maintained after Co incorporation. However, the systematic shift of the ZnO-related reflections toward higher 2θ values indicates a decrease in the interplanar spacing according to Bragg's law. As summarized in Table 1, the d-spacing of the (100) plane decreases from 2.81 Å for undoped ZnO to 2.80 Å for ZnO:Co, while the d-spacing of the (002) plane decreases from 2.62 Å to 2.61 Å. This behavior suggests a slight contraction of the ZnO lattice, which may be associated with the incorporation of Co ions into the ZnO crystal structure and/or with residual strain generated during film growth. Similar effects have been reported for Co-doped ZnO systems, where Co incorporation can modify lattice parameters, induce strain, affect crystallite size, and generate structural disorder while preserving the ZnO-based wurtzite framework at suitable dopant concentrations [20–22].

Table 1. Structural parameters obtained from the XRD analysis of undoped ZnO and ZnO:Co thin films deposited on titanium substrates.

Plane	2 θ ZnO (°)	2 θ ZnO:Co (°)	FWHM (°)	FWHM (°)	d ZnO (Å)	d ZnO:Co (Å)	D ZnO (nm)	D ZnO:Co (nm)
(100)	31.79	31.91	0,036	0,94	2.81	2.8	229.45± 63.74	8.79 ± 0.09
(002)	34.19	34.26	0,24	0,23	2.62	2.61	34.63 ± 1.44	36.14 ± 1.57
(101)	36.09	36.14	0,48	0,31	2.48	2.48	17.41 ± .036	29.96 ± 0.87

The apparent crystallite size was estimated using the Scherrer equation $D = \frac{K\lambda}{\beta \cos\theta}$. For the most representative ZnO (002) reflection, the crystallite size is approximately 34.63± 1.44 nm for the undoped ZnO film and 36.14 ± 1.57 nm for the ZnO:Co film. These close values suggest that Co incorporation does not significantly modify the coherent crystalline domain size along the direction associated with the (002) plane. In contrast, the apparent crystallite sizes obtained from the (100) and (101) reflections exhibit larger and plane-dependent variations. For the (100) reflection, the estimated crystallite size decreases markedly from 229.45 ± 63.74 nm for ZnO to 8.79 ± 0.09 nm for ZnO:Co, whereas the value derived from the (101) reflection increases from 17.41 ± 0.36 nm to 26.96 ± 0.87 nm after Co incorporation. These results should be interpreted cautiously, particularly for the (100) reflection, because the unusually small FWHM (Full Width at Half Maximum) measured for the undoped ZnO film may be comparable to the instrumental broadening and highly sensitive to the peak-fitting procedure. Therefore, the calculated values should be regarded as apparent coherent-domain sizes rather than absolute grain sizes.

In addition, no intense diffraction peaks associated with crystalline Co, CoO, or Co₃O₄ phases are clearly observed in the analyzed angular region. This result suggests that, within the detection limit of conventional XRD, Co incorporation does not lead to the formation of detectable secondary crystalline cobalt-related phases. Nevertheless, due to the weak intensity and broad nature of the ZnO-related reflections, the presence of minor amorphous or poorly crystalline secondary phases cannot be completely ruled out by XRD alone. This limitation is especially relevant in Co-doped ZnO thin films, since previous studies have shown that XRD may indicate only the ZnO wurtzite phase even when complementary vibrational techniques reveal local disorder or cobalt oxide-related contributions [23]. Therefore, the XRD results should be interpreted as evidence of the average long-range crystallographic order, while complementary techniques such as Raman spectroscopy, FTIR, EDX, XPS, or grazing-incidence XRD are required to further evaluate local structural disorder, chemical state, and dopant distribution [23,24].

3.2. Raman Spectroscopy

Raman spectroscopy was performed over the spectral range of 100–500 cm⁻¹ to complement the structural information obtained from XRD and to evaluate the local vibrational order of the films. The Raman spectra of the undoped ZnO and ZnO:Co thin

films are presented in Fig. 2. The undoped ZnO thin film exhibits a characteristic vibrational mode close to the E_2 (high) mode of wurtzite ZnO, located near $433\text{--}439\text{ cm}^{-1}$. This result indicates that, despite the broad diffraction response observed by XRD, the film preserves local vibrational features associated with the hexagonal ZnO structure. Similar Raman modes have been reported for ZnO-based materials and are commonly associated with the wurtzite lattice vibration response [12,23,24]. In contrast, the ZnO:Co thin film shows a modified Raman response, including a broader contribution centered around 475 cm^{-1} . In contrast, the ZnO:Co thin film shows a modified Raman response, including a broader contribution centered around 475 cm^{-1} . This additional feature may be associated with Co-induced lattice disorder and defect-activated vibrational contributions, as previously reported in Raman studies of Co-doped ZnO systems [23].

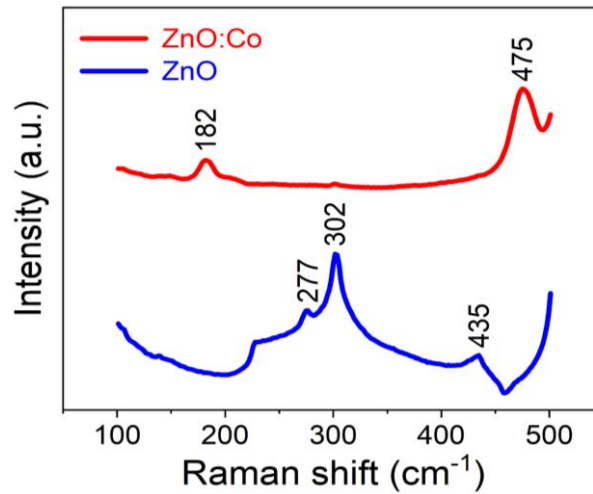


Figure 2. Raman spectra of undoped ZnO and ZnO:Co thin films, showing the characteristic vibrational response of the ZnO matrix and the modifications induced by Co incorporation.

3.3. FTIR Spectroscopy

The FTIR spectra of the undoped ZnO and ZnO:Co thin films are shown in Fig. 3. These spectra further confirm differences in the vibrational response of both samples. The undoped ZnO film exhibits characteristic absorption bands in the low-wavenumber region, particularly near 600 and 399 cm^{-1} , which can be associated with Zn–O stretching vibrations in the wurtzite ZnO lattice. Similar Zn–O-related infrared bands have been reported in ZnO and Co-doped ZnO systems, confirming the formation of the ZnO network and the presence of metal–oxygen vibrational modes [25,26].

For the ZnO:Co thin film, the absorption bands appear shifted and broadened, with contributions near 570 , 860 , and 983 cm^{-1} . The modification of these features suggests a perturbation of the Zn–O–Zn network due to Co incorporation, lattice distortion, and defect-related metal–oxygen vibrations. In ZnO:Co systems, FTIR band shifts and broadening are commonly associated with changes in local bonding configuration, dopant-induced disorder, and modifications in the metal–oxygen vibrational environment [12,25,26].

Nevertheless, the higher-wavenumber bands should be interpreted cautiously, since they may also include contributions from surface species, substrate effects, adsorbed groups, or local disorder. Overall, the FTIR results are consistent with the Raman observations

and indicate that Co incorporation modifies the local bonding configuration of the ZnO matrix.

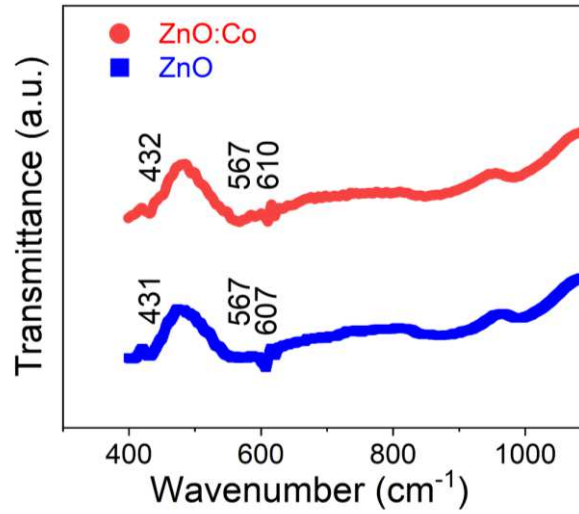


Figure 3. FTIR spectra of undoped ZnO and ZnO:Co thin films, showing the vibrational bands associated with Zn–O bonding and the spectral modifications produced by Co doping.

The structural results indicate that cobalt incorporation modifies the ZnO thin films without destroying the hexagonal wurtzite structure. The ZnO-related XRD reflections shift slightly toward higher (2θ) values after Co addition, together with a small reduction in interplanar spacing. This behavior suggests lattice contraction and/or residual strain induced during film growth, as previously reported for transition-metal-doped ZnO systems [15,20–22]. The similar crystallite sizes obtained from the (002) reflection indicate that Co does not strongly modify the coherent crystalline domain along this direction. However, the larger variations observed for the (100) and (101) planes should be interpreted cautiously because of the weak peak intensity, substrate contribution, and uncertainty associated with the Scherrer estimation.

No intense diffraction peaks corresponding to metallic Co, CoO, or Co₃O₄ were detected, suggesting that no dominant crystalline Co-rich secondary phase is formed within the XRD detection limit. Nevertheless, minor amorphous or poorly crystalline cobalt-containing regions cannot be completely excluded. This limitation is relevant because XRD mainly probes long-range order, whereas local disorder and bonding modifications may be more clearly detected by Raman and FTIR spectroscopy [23,24].

The vibrational results support the presence of local structural changes. Undoped ZnO exhibits a Raman contribution close to the characteristic (E_2)(high) mode of wurtzite ZnO, whereas ZnO:Co shows a broader band around 475 cm⁻¹. This feature may be associated with Co-induced lattice perturbations, defect-activated modes, or local structural disorder [12,23,24]. Similarly, the FTIR bands associated with Zn–O vibrations become shifted and broadened after Co incorporation, indicating changes in the local metal–oxygen bonding environment. However, the higher-wavenumber bands may also contain contributions from surface species or substrate-related effects and should therefore be interpreted cautiously [12,25,26].

3.3. XPS

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface elemental composition and chemical states of the ZnO:Co thin film. The survey spectrum shown in Fig. 4a confirms the presence of Zn, O, C, and Co on the sample surface. The Zn 2p and O 1s signals are associated with the ZnO matrix, whereas the comparatively weak Co 2p signal is consistent with the low cobalt concentration previously determined by EDX. The C 1s signal located at approximately 284.8 eV is mainly attributed to adventitious carbon contamination commonly found on surfaces exposed to ambient

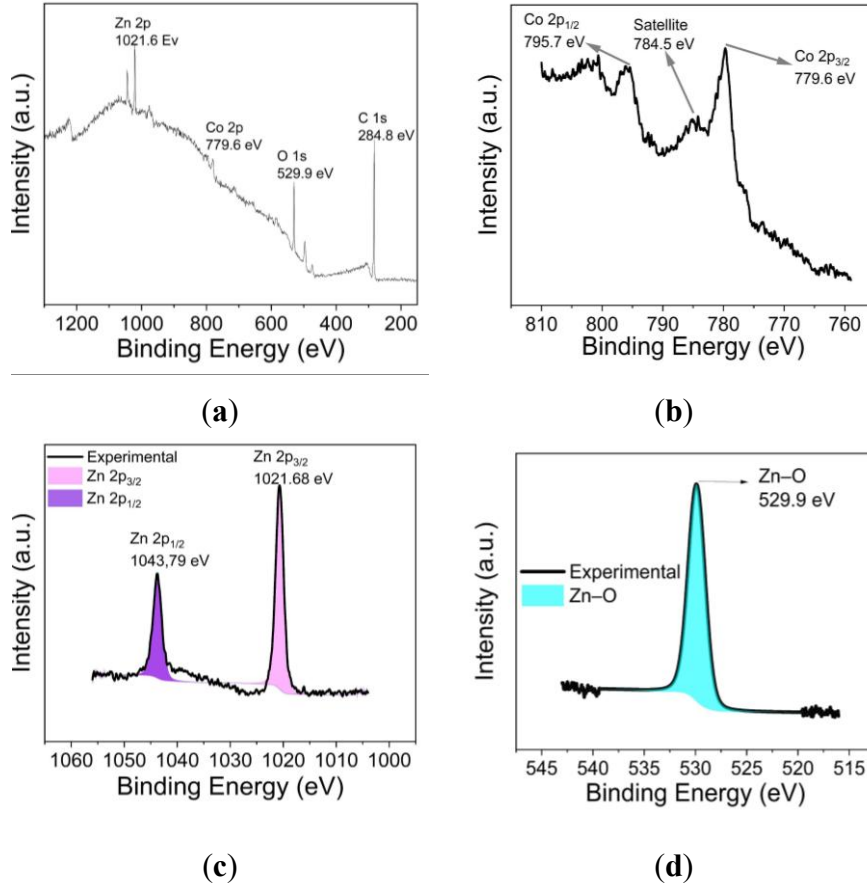


Figure 4. XPS characterization of the ZnO:Co thin film: (a) survey spectrum confirming the presence of Zn, O, C, and Co; (b) high-resolution Co 2p spectrum showing the Co 2p_{3/2}, satellite, and Co 2p_{1/2} features; (c) high-resolution O 1s spectrum and fitted Zn–O component; and (d) high-resolution Zn 2p spectrum showing the Zn 2p_{3/2} and Zn 2p_{1/2} doublet.

The high-resolution Co 2p spectrum shown in Fig. 4b exhibits contributions centered at approximately 779.6 and 795.7 eV, assigned to the Co 2p_{3/2} and Co 2p_{1/2} components, respectively. The corresponding spin–orbit splitting is approximately 16.1 eV. In addition, a satellite feature is observed at approximately 784.5 eV, located about 4.9 eV above the Co 2p_{3/2} signal. The presence of the Co 2p doublet together with the satellite contribution confirms that cobalt is present in an oxidized chemical environment. Despite the low Co concentration and the relatively broad spectral features, the position and spectral characteristics of these contributions are consistent with cobalt incorporated into an oxide environment within the ZnO-based matrix. Therefore, the Co 2p spectrum supports the incorporation of oxidized Co species into the semiconductor matrix, although the coexistence of different local Co environments cannot be completely excluded.

The high-resolution O 1s spectrum presented in Fig. 4c is dominated by a component centered at approximately 529.9 eV, assigned to lattice oxygen bonded to Zn in the ZnO structure. The predominance of this contribution indicates that oxygen is mainly incorporated into the oxide lattice through Zn–O bonds. No additional high-binding-energy component associated with hydroxyl groups, adsorbed oxygen species, or oxygen-related defects was included in the present fitting.

The Zn 2p spectrum shown in Fig. 4d displays the characteristic Zn 2p_{3/2} and Zn 2p_{1/2} doublet located at 1021.68 and 1043.79 eV, respectively. The resulting spin–orbit splitting of approximately 22.11 eV is characteristic of Zn²⁺ in a ZnO chemical environment. These results indicate that zinc remains predominantly in its divalent oxidation state after cobalt incorporation.

No intense additional Co-related contributions attributable to a dominant segregated cobalt-rich phase are clearly observed. Therefore, together with the XRD, Raman, and EDX results, the XPS measurements support the presence of cobalt as a dilute dopant in the ZnO-based film rather than as a major secondary cobalt oxide phase.

Complementing the structural and vibrational evidence, XPS and EDX provide the incorporation of cobalt into the ZnO-based film. EDX detects approximately 0.84 wt.% Co, while XPS shows that Zn remains predominantly in the Zn²⁺ state and that O is mainly present as lattice oxygen bonded to Zn. The Co 2p spectrum, including the spin–orbit components and satellite feature, indicates that cobalt is present in an oxidized environment. However, because of the low Co concentration and broad spectral features, its exact oxidation state cannot be determined unambiguously. Overall, the XPS, EDX, and XRD results suggest that cobalt is present as a dilute component rather than as a dominant segregated phase.

Overall, the XPS, EDX, and XRD results suggest that cobalt is present as a dilute component rather than as a dominant segregated phase. Beyond these structural and chemical modifications, Co incorporation also produces a clear change in surface morphology. The undoped ZnO film exhibits a relatively compact and continuous surface, whereas ZnO:Co shows a rougher and more granular morphology with agglomerated regions. These differences indicate that cobalt modifies nucleation, surface diffusion, and grain coalescence during sputtering. Similar changes in grain distribution and surface roughness have been reported for metal-doped ZnO films [3,25,26].

3.4. Morphological Characterization

The surface morphology of the undoped ZnO and ZnO:Co thin films was analyzed by scanning electron microscopy, as shown in Fig. 5.a, 5.b The undoped ZnO film in 36kx and 70kx magnification, presents a relatively compact and granular surface with smooth coalesced regions. This morphology suggests limited grain development and relatively homogeneous coverage of the titanium substrate.

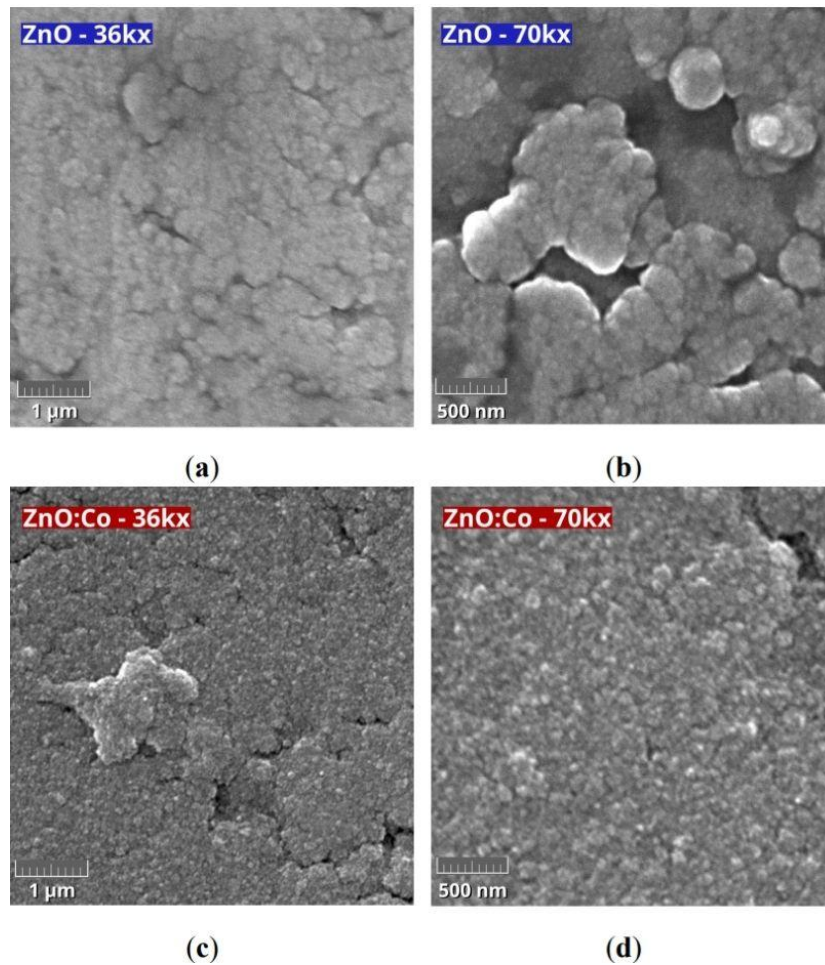


Figure 5. SEM micrographs of undoped ZnO and ZnO:Co thin films deposited on titanium substrates, showing the morphological changes associated with Co incorporation, for 36kx and 70kx magnifications.

In contrast, the ZnO:Co thin film exhibits a rougher, granular, and heterogeneous surface, characterized by smaller grain size, less cracking, and greater coalescence.

The incorporation of Co appears to modify the growth kinetics of the film, promoting changes in nucleation, grain formation, and surface coalescence. Similar morphological modifications have been reported in metal-doped ZnO systems, where dopant incorporation affects crystallite size, particle distribution, surface roughness, and microstructural homogeneity [3,25,26].

This morphological evolution is consistent with the structural and vibrational evidence obtained from XRD, Raman, and FTIR analyses, supporting the conclusion that Co incorporation increases local disorder and modifies the organization of the ZnO matrix. In this sense, the SEM observations reinforce the idea that the structural perturbation induced by Co is not limited to the crystallographic scale but also affects the surface growth morphology of the deposited thin films.

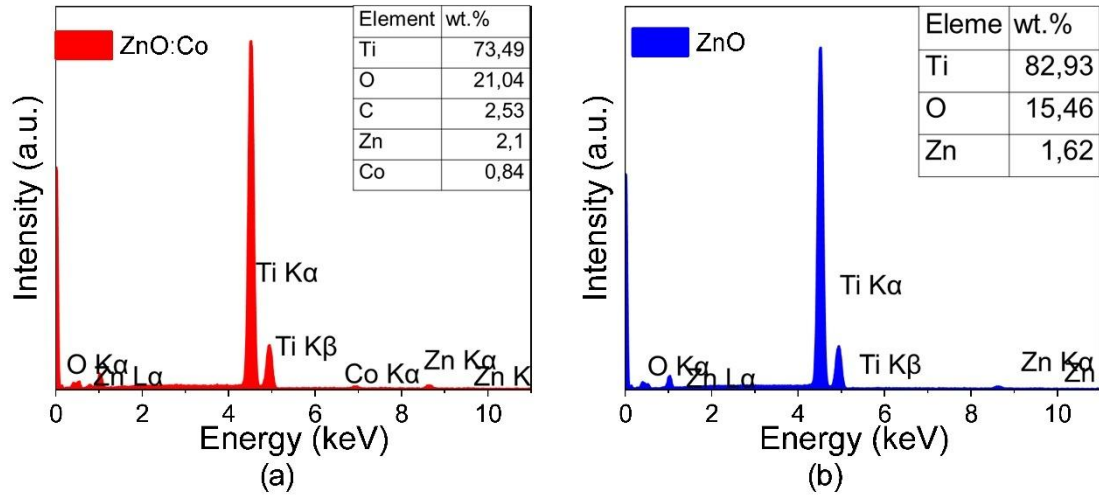


Figure 6. EDX spectra and elemental composition of (a) ZnO/Ti and (b) ZnO:Co/Ti thin films

The EDX spectra of the ZnO/Ti and ZnO:Co/Ti samples confirm the presence of Zn and O associated with the ZnO-based film, together with a strong Ti signal arising from the substrate. In the doped sample, Co is additionally detected with a concentration of 0.84 wt.%, evidencing the incorporation of cobalt into the ZnO matrix. The EDX spectra of the ZnO/Ti and ZnO:Co/Ti samples confirm the presence of Zn and O associated with the ZnO-based film, together with a strong Ti signal arising from the substrate. In the doped sample, Co is additionally detected with a concentration of 0.84 wt.%, evidencing the incorporation of cobalt into the ZnO matrix. After excluding the Ti contribution from the substrate and renormalizing the remaining elemental concentrations to 100%, the relative Co content increases to 3.17 wt.%.

3.5. Optical Characterization

The optical properties (bandgap, thickness, refraction index, extinction coefficient) of ZnO and ZnO:Co thin films were evaluated from UV–Vis–NIR transmittance measurements following the Bhattacharyya method for thin films [27] and applying the Tauc model assuming a direct allowed electronic transition [28]. The undoped ZnO film exhibits an optical band gap of approximately 3.16 eV (Fig. 7b), which is consistent with a direct-transition ZnO-based semiconductor and suggests a relatively preserved electronic structure. ZnO is widely reported as a wide direct band gap semiconductor, and its optical response can be strongly affected by dopants, film morphology, defect density, and deposition method [3,19,20].

In contrast, the ZnO:Co thin film shows a reduced optical band gap of approximately 2.7 eV (Fig. b), indicating a red shift of the absorption edge toward lower photon energies. This band-gap narrowing may be associated with Co incorporation, structural disorder, oxygen vacancies, and the formation of localized defect states within the forbidden gap. Similar red shifts and band-gap reductions have been reported in Co-doped and Mn/Co-doped ZnO systems, where transition-metal incorporation modifies the electronic structure and enhances absorption in the visible region [12,15,21].

The reduction of the optical band gap can also be related to sp–d exchange interactions between the ZnO band electrons and the localized d-electrons of Co^{2+} ions, as well as to

defect-induced electronic states generated within the forbidden gap [20,21]. These defect-related states can modify the electronic structure of the ZnO matrix and facilitate optical transitions at lower energies. Therefore, the UV–Vis-NIR results are consistent with the structural, vibrational, and morphological evidence, indicating that Co incorporation modifies both the local structure and the electronic configuration of the ZnO thin films.

The Bhattacharyya method allows to computationally determine the optical thickness of thin films through an iterative procedure in which the theoretical transmittance spectrum is systematically adjusted by varying the film thickness until the quantity $\Delta T = |T_{exp} - T_{calc}|$ is minimized. The minimum of ΔT may correspond to the thickness value for which the optical interference fringes of the calculated spectrum best reproduce those of the experimental one [27], making it a physically meaningful and self-consistent estimation. This procedure yields a thickness of ~ 100.57 nm for the ZnO thin film and ~ 93.04 nm for the ZnO:Co thin film (Fig. 7c). The method also allows the determination of the refractive index and extinction coefficient spectra (Fig. 7d), from which the real and imaginary parts of the dielectric function can be obtained (Fig. 8a) as:

$$\varepsilon_1 = n^2(\lambda) - k^2(\lambda) \quad (1)$$

$$\varepsilon_2 = 2n(\lambda)k(\lambda) \quad (2)$$

Following the simplification proposed by Bhattacharyya, in which the damping factor γ is neglected ($\gamma = 0$), the real part of the dielectric function reduces from:

$$\varepsilon_1 = \varepsilon_\infty - (\varepsilon_\infty \omega_p^2) \left(\frac{1}{\omega^2} + \gamma^2 \right) \quad (3)$$

To

$$\varepsilon_1 = \varepsilon_\infty - (\varepsilon_\infty \omega_p^2) \left(\frac{1}{\omega^2} \right) \quad (4)$$

This expression is linear in $1/\omega^2$, which allows ε_∞ and ω_p^2 to be extracted directly from a linear regression of ε_1 as a function of $1/\omega^2$ (Fig. 8b), where the intercept yields the high-frequency dielectric constant ε_∞ and the slope corresponds to the term $(-\varepsilon_\infty \omega_p^2)$. The plasma frequency ω_p is proportional to the free carrier density N through:

$$\omega_p^2 = \frac{Nq^2}{\varepsilon_0 m^*} \quad (5)$$

where q is the electron charge, ε_0 is the permittivity of free space, m^* is the electron effective mass for ZnO ($m^* = 0.24m_0$), and m_0 is the free electron mass [29].

An estimate of refraction index (n) is shown on Table 2, extinction coefficient (k), real and imaginary parts of the dielectric function for ZnO and ZnO:Co samples.

Table 2. Estimation of refraction index (n) , extinction coefficient (k) with real and imaginary parts of the dielectric function for ZnO and ZnO:Co samples.

λ (nm)	ZnO				ZnO:Co			
	n	k	ε_1	ε_2	n	k	ε_1	ε_2
350	1.89	0.12	3.59	0.45	1.78	0.20	3.15	0.73
600	1.91	0.04	3.63	0.15	1.88	0.12	3.53	0.46
900	1.89	0.06	3.58	0.24	1.90	0.15	3.60	0.57
1100	1.91	0.08	3.64	0.30	1.96	0.18	3.82	0.73

Table 3 summarizes the values of plasma frequency ω_p , high-frequency dielectric constant ε_∞ , and carrier density N obtained for the ZnO and ZnO:Co thin films using the Bhattacharyya and Tauc methods.

In the case of the ZnO:Co thin film, the linear regression of ε_1 as a function of $(1/\omega^2)$ yielded a positive slope, which is physically inconsistent with the Drude model framework underlying the Bhattacharyya method, and consequently prevented the extraction of ω_p and N for this sample.

The behavior of ε_1 for the ZnO:Co film reveals two distinct spectral regions. In the high-frequency region ($1/\omega^2 < \sim 1 \times 10^{-31} \text{ s}^2\text{rad}^{-2}$), ε_1 increases rapidly from ~ 1.9 to ~ 3.6 , a behavior characteristic of interband electronic transitions [30], consistent with the onset of optical absorption in this spectral range. In the low-frequency region selected for the linear fit ($1/\omega^2 > \sim 1 \times 10^{-31} \text{ s}^2\text{rad}^{-2}$), ε_1 increases slowly from ~ 3.5 to ~ 3.8 , resulting in a positive slope in the linear regression.

Table 3. Estimation of bandgap E_g , thickness d , plasma frequency ω_p , high-frequency dielectric constant ε_∞ , and carrier density N calculated using Bhattacharyya and Tauc method for ZnO and ZnO:Co thin films deposited with $T_s = 293 \text{ K}$.

$P_{\text{ZnO}}(\text{W})$	$P_{\text{Co}}(\text{W})$	$E_g(\text{eV})$	$d(\text{nm})$	ε_∞	$\omega_p(10^{14}\text{rad s}^{-1})$	$N(\text{cm}^{-3})$
100	0	3.16	100.6	3.65	2.31	3.85×10^{18}
100	50	2.7	93.04	3.48	-	-

This differential response between the ZnO and ZnO:Co films is attributed to the effect of Co in modifying the electronic band structure, which was evidenced by the reduction of the optical bandgap from 3.16 eV to 2.7 eV. Despite these effects, the compositional results (EDXS) show that the ZnO:Co thin film contains 3.17 wt.% Co, remaining within the dilute regime and preserving the semiconductor characteristics of interest.

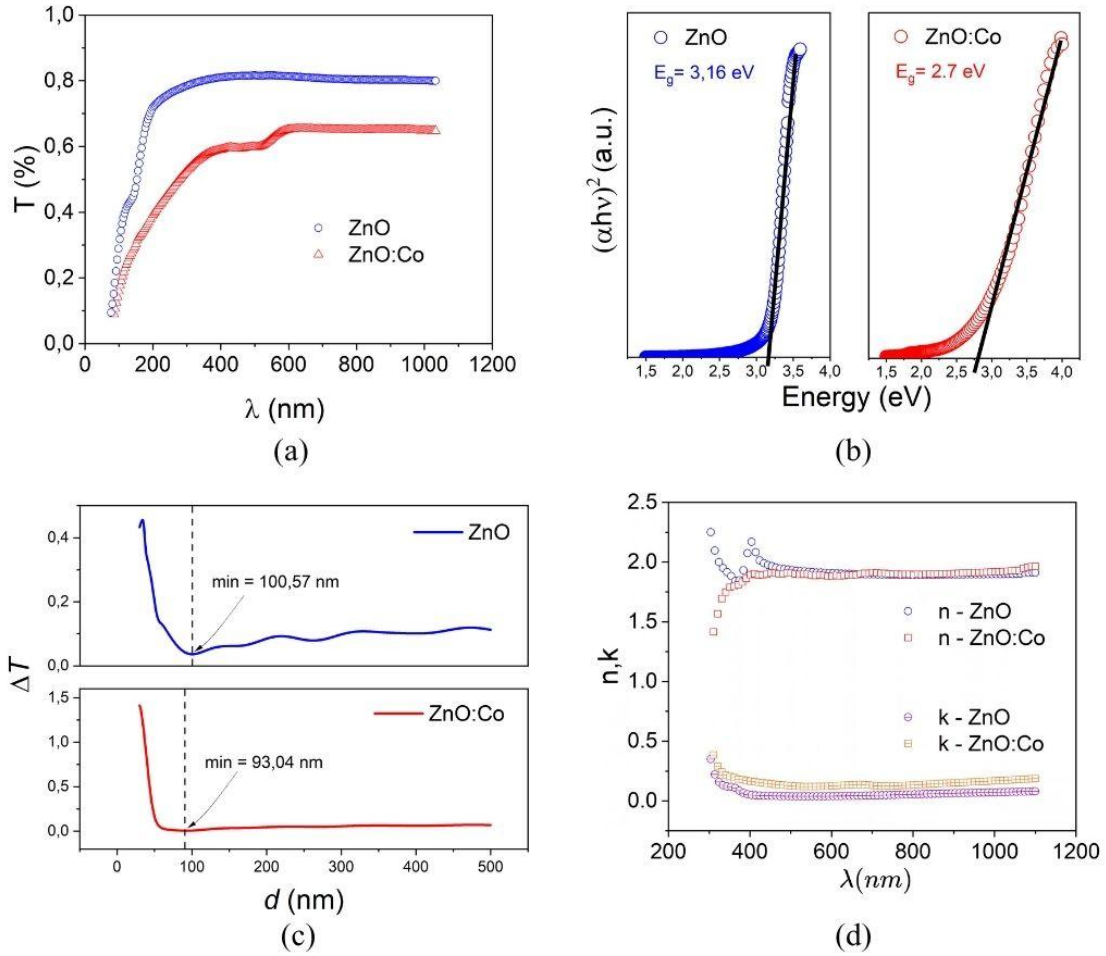


Figure 7. Optical properties of ZnO and ZnO:Co thin films with 100W of target power and 293K of substrate temperature. a) Transmittance spectra, b) Tauc plot for direct bandgap estimation, c) estimated thickness based on the Bhattacharyya method, d) refractive index and extinction coefficient estimation.

Optical characterization corroborates the structural, morphological, and electrical modifications induced by Co in the ZnO lattice. The undoped ZnO film exhibits an optical band gap of approximately 3.16 eV, which falls within the range reported using the Tauc method for ZnO [38]. The incorporation of cobalt induces a redshift to 2.7 eV, significant for its concentration of 3.17 wt.% with respect to values reported for 3% concentrations using chemical techniques, such as 3.09 eV [37] and 3.25 eV [38]; this is attributed to the low thickness of the thin film and to the nature of the deposition technique employed. The band gap reduction can be fundamentally attributed to two mechanisms: first, the strong sp-d exchange interactions between the electrons of the ZnO matrix and the localized d electrons of the incorporated Co^{2+} ions, which alter the band structure; second, as confirmed by the structural and morphological analyses, Co doping introduces disorder in the ZnO lattice, promoting the formation of oxygen vacancies, a phenomenon that favors the emergence of intermediate energy levels that enable lower-energy optical transitions, thereby enhancing the absorption level in the visible region of the spectrum.

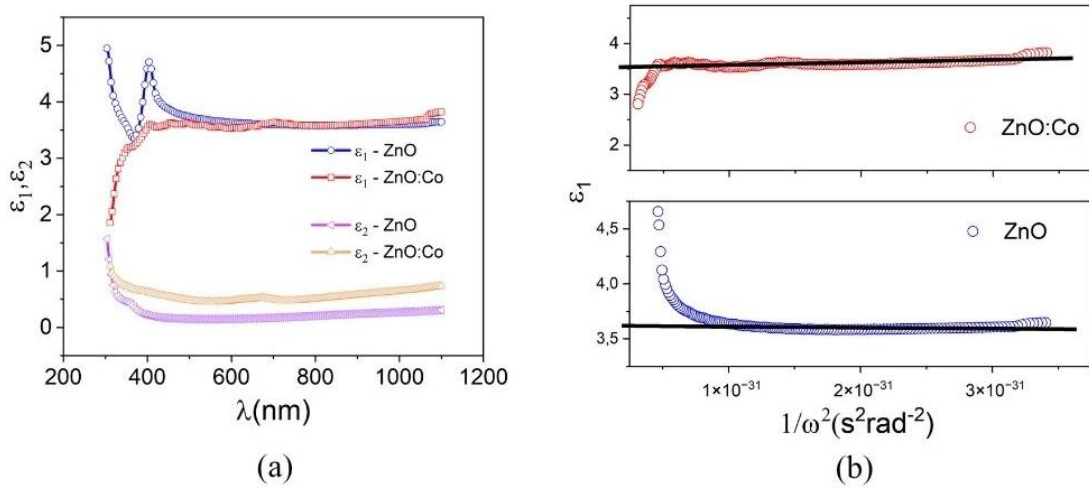


Figure 8. Optical properties of ZnO and ZnO:Co thin films with 100W of target power and 293K of substrate temperature. a) Estimation of real and imaginary parts of dielectric function and b) plasma frequency estimation.

3.6. Electrical Characterization

The cycling endurance behavior of the ZnO and ZnO:Co thin-film devices was evaluated through the evolution of the high-resistance state (HRS) and low-resistance state (LRS) as a function of switching cycles, as shown in Fig. 7. The ZnO (Fig. 6a) device exhibits a narrow resistance window, with the LRS remaining close to 1 Ω and the HRS fluctuating between approximately 5 and 8 Ω . This weakly defined separation suggests limited resistive switching stability, possibly associated with structural disorder, interfacial effects, nonuniform transport pathways, or incomplete formation of conductive paths. In contrast, the ZnO:Co (Fig. 6b) device shows a clearer separation between HRS and LRS, with resistance values in the megaohm range, indicating that Co incorporation strongly modifies the electrical transport within the ZnO matrix.

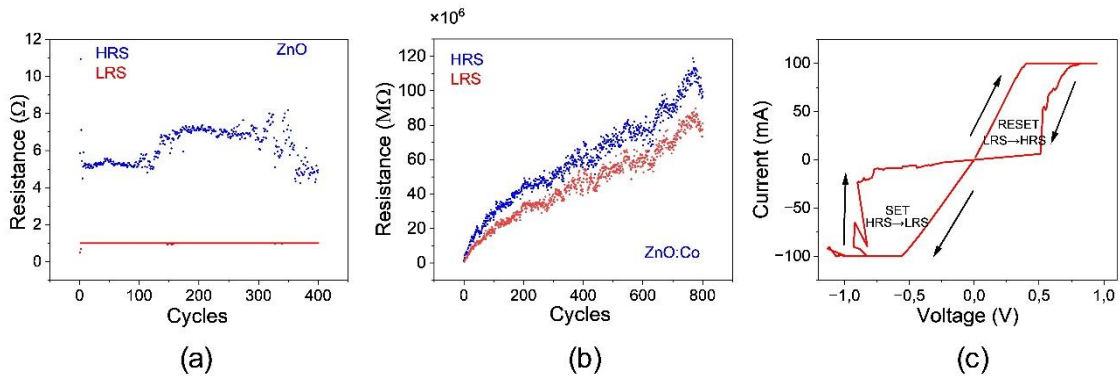


Figure 9. Resistive-switching characteristics of the ZnO and ZnO:Co thin-film devices: endurance behavior of the high-resistance state (HRS) and low-resistance state (LRS) as a function of switching cycles for (a) ZnO and (b) ZnO:Co, and (c) representative current–voltage characteristic of the ZnO:Co device. The arrows indicate the voltage-sweep direction.

This behavior can be attributed to localized electronic states, defect-related trapping centers, and oxygen-vacancy-assisted conduction paths. In ZnO-based RRAM devices, resistive switching is commonly related to the formation and rupture of conductive

filaments mediated by oxygen vacancies and defect migration [7]. Moreover, suitable Co doping has been reported to improve the memory window and switching stability of ZnO-based devices [31]. Although the ZnO:Co sample exhibits improved resistive state separation, the progressive increase of both HRS and LRS with cycling suggests resistance drift, likely caused by defect redistribution or gradual modification of conductive filaments during repeated switching.

The representative current–voltage characteristic of the ZnO:Co device shown in Fig. 7c exhibits a pronounced hysteresis loop with resistance transitions occurring at opposite voltage polarities. During the negative-voltage sweep, an abrupt increase in the current magnitude is observed at approximately -0.9 V, corresponding to the SET transition from HRS to LRS. Conversely, during the positive-voltage sweep, the current decreases abruptly near $+0.5$ V, indicating the RESET transition from LRS to HRS. The occurrence of SET and RESET processes under opposite bias polarities is consistent with bipolar resistive-switching behavior. This response may be associated with the electric-field-driven redistribution of oxygen vacancies and the reversible formation and disruption of localized conductive pathways within the ZnO:Co film

Another electrical property evaluated was the temperature (T) dependence of the electrical conductivity (σ) as shown on Fig. 8, for the ZnO and ZnO:Co samples. The measurements were performed under a 5 ± 0.0057 V bias using the two-probe configuration [32]. Conductivity was determined indirectly from the current response induced by the applied voltage and calculated by considering the sample geometry through the relation:

$$\sigma = \frac{1}{\rho} = \frac{L}{R \cdot A} = \frac{I \cdot L}{V \cdot t \cdot w} \quad (6)$$

where I is the measured current, L is the distance between contacts, V is the applied voltage, t is the sample thickness, and w is the sample width. It's important to note that the thickness employed was the obtained from the optical transmittance analysis previously reported in this work (See Tab. 3, $\sigma_{\text{ZnO}} = 100.57$ nm and $\sigma_{\text{ZnO:Co}} = 93.04$ nm).

Under these conditions, a pronounced conductivity minimum, equivalent to a maximum in resistivity, is identified at $T = 151.35 \pm 0.001$ K for ZnO and at $T = 213.15 \pm 0.001$ K for ZnO:Co. At these temperatures, the minimum conductivity reaches $\sigma_{\text{min}} = 1.62 \pm 0.05$ S·cm⁻¹ for ZnO and $\sigma_{\text{min}} = 3.51 \times 10^{-8} \pm 0.17 \times 10^{-8}$ S·cm⁻¹ for ZnO:Co. Above this temperature range, both samples exhibited a continuous increase in conductivity, which is consistent with a thermally activated transport regime commonly reported for polycrystalline ZnO-based semiconductors [33,34]. Furthermore, this behavior may also be associated with the donor defects, such as oxygen vacancies, Zinc interstitials, or interstitial Oxygen, a mechanism previously reported in some transport studies of polycrystalline ZnO and ZnO:Co [33,35,36].

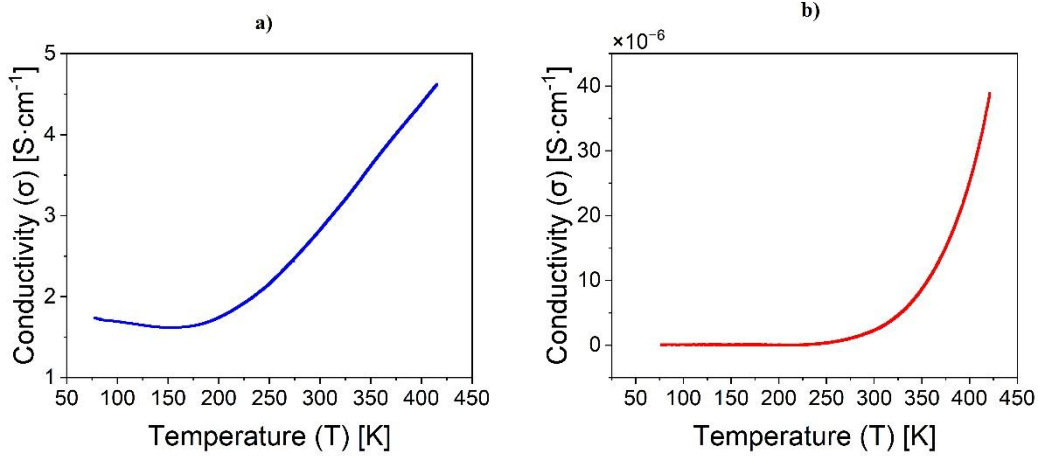


Figure 10. Electrical measurements of conductivity, (a) ZnO and (b) ZnO:Co.

To further analyze the transport mechanism, data were represented in Arrhenius plot ($\ln \sigma$ as a function of $1000/T$) as shown in Fig. 11 for the ZnO and ZnO:Co films. The Arrhenius formalism was originally introduced to describe the temperature dependence of chemical reaction rates, nevertheless it has been widely extended to thermally activated transport processes in semiconducting materials [37] through the relation:

$$\sigma = \sigma_0 \cdot e^{(-E_a / k_B \cdot T)} \quad (7)$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. By linearizing this expression yields:

$$\ln(\sigma) = \ln(\sigma_0) - \frac{E_a}{k_B \cdot T} \quad (8)$$

Which indicates that an Arrhenius representation should show a linear dependence in the temperature range where thermally activated conduction dominates. In this context, the linear fit was found to reproduce satisfactorily the experimental data in the higher-temperature region as evidenced in the insets of Fig. 11.

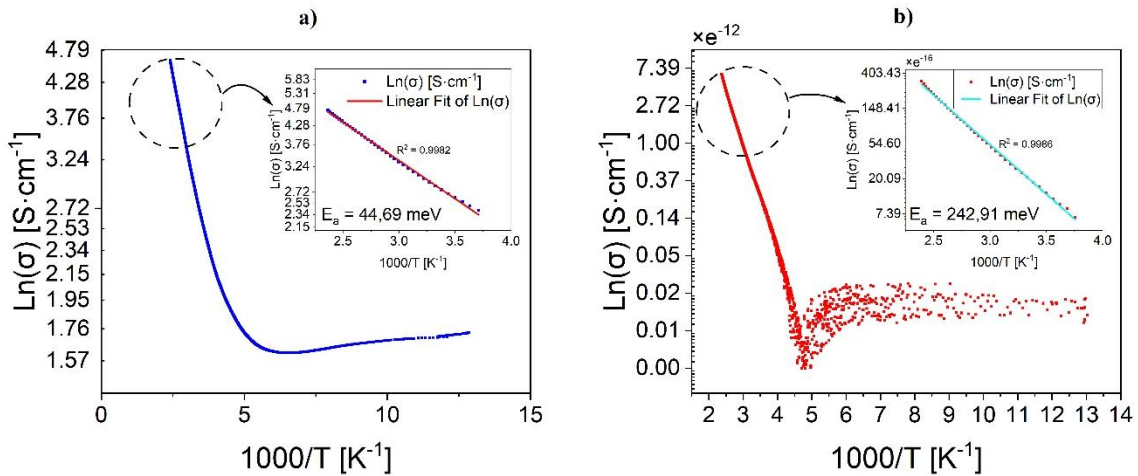


Figure 11. Electrical measurements of conductivity of (a) ZnO and (b) ZnO:Co. From the slope (m) of the fitted liner function and the expression:

$$E_a = -1000 \cdot k_B \cdot m. \quad (8)$$

An activation energy of $E_a = 44.7 \pm 0.004$ meV was determined for the ZnO film. The same analysis was performed for the ZnO:Co film which resulted in an activation energy of 242.91 ± 0.21 meV.

These structural, morphological and optical differences are reflected in the robustness of the HRS and LRS states. The undoped ZnO device exhibits a narrow resistance window, with the LRS close to 1Ω and the HRS between approximately 5 and 8Ω . Although both states can be distinguished, their limited separation indicates weak resistive-state differentiation. The compact morphology of the undoped film may favor highly conductive paths that remain active in both states, reducing the resistance contrast.

In contrast, the ZnO:Co device exhibits a clearer separation between HRS and LRS, with resistance values in the megaohm range. This wider resistance window suggests that Co incorporation strongly modifies the conductive landscape of the ZnO matrix. Structural disorder, localized trapping centers, grain boundaries, and defect-assisted conductive paths may contribute to the improved distinction between both states. In ZnO-based RRAM devices, HRS/LRS stability is commonly related to the formation and modification of defect-mediated conductive pathways, particularly those involving oxygen vacancies [7]. Suitable Co incorporation has also been reported to improve the memory window and cycling stability of ZnO-based devices [31].

Despite the improved HRS/LRS separation, both resistance states progressively increase during cycling in the ZnO:Co device. This resistance drift suggests that the internal conductive network continues to evolve under repeated electrical operation, possibly because of defect redistribution, changes in trapping-site occupancy, or gradual modification of the conductive paths [7]. Nevertheless, the separation between HRS and LRS remains visible, indicating that the resistive window is preserved over the evaluated cycles.

Overall, dilute Co incorporation produces a more heterogeneous ZnO matrix and improves the distinction between HRS and LRS compared with undoped ZnO. However, the progressive drift of both resistance states indicates that further control of defect distribution and microstructural homogeneity is required to achieve greater long-term cycling stability.

The I-V and temperature dependent conductivity measurements provide complementary information on the electrical transport mechanisms of the ZnO and ZnO:Co films. Whereas the I-V response highlights the importance of structure in differentiating between HRS and LRS states and how it affects the stability of this resistive window; the conductivity quantifies the thermal energy required for charge carriers to become mobile.

Although each characterization technique provides distinct information regarding the behavior of the sample, an integrated analysis, such as that proposed in this study, enables the extraction of more meaningful data and facilitates the examination of interconnected mechanisms. This is evidenced by the relationship between film thickness and electrical conductivity that it's predominantly governed by surface-related contributions on a thermally activated transport regime, in which charge carriers gain sufficient thermal energy to be promoted from localized defect states into the conduction band. This behavior is commonly reported in polycrystalline ZnO-based semiconductors and has

been associated with the thermal ionization of shallow donor defects such as oxygen vacancies, zinc interstitials, or interstitial oxygen species [33,34].

The two-probe configuration is a consolidated technique for obtaining a reasonable estimate of the electrical conductivity from the current measured under an applied bias. However, the reported values should be interpreted as effective conductivities normalized according to the film geometry, since both contact resistance and the associated with the interface between electrode and film may also contribute to the measured response. A common approach to mitigate these contributions is to extend the measurement methodology to a four-probe configuration [32,39]. Despite these limitations, the overall analysis of the conductivity behavior within the Arrhenius framework, as described in Section 3.6, makes it possible to identify that an thermally activation conduction process governs the electrical transport in the high temperature regime. This behavior is clearly evidenced by the linear dependence of $\ln \sigma$ on $1/T$, confirming that conduction mediated by thermally excited charge carriers predominates within this temperature range.

Although Co doping is found to reduce the electrical conductivity of ZnO across the measured temperature range, the thermally activated transport behavior at high temperature is preserved, and the activation energy remains within the same order of magnitude as undoped ZnO. This suggests that the underlying conduction mechanism thermal excitation of carriers from donor states into the conduction band is not fundamentally altered by Co incorporation. However, the increase in grain size supported by SEM measurements is expected to raise the potential barrier height at grain boundaries, thereby modulating carrier transport through percolation and diffusion mediated pathways across these interfaces [33]. Consequently, while the overall transport regime remains thermally activated, the specific conduction channels appear to be governed by the formation and rupture of conductive filament paths, together with charge carrier hopping through defect related trapping centers whose density is enhanced by the dopant which is consistent with the slightly higher activation energy observed in Co-doped ZnO relative to the undoped film.

5. Conclusions

This study presents a comprehensive comparative analysis of ZnO and ZnO:Co thin films synthesized by DC magnetron co-sputtering. Structural characterization by XRD, Raman, and FTIR confirms that Co incorporation (approx. 3.17 wt.%) preserves the hexagonal wurtzite structure of the ZnO matrix and Co-oxide phases are not observed even though inducing lattice contraction, increased local disorder, and a transition to a rougher, granular surface morphology.

The incorporation of cobalt effectively narrows the optical band gap from 3.16 eV to 2.70 eV, extending the optical absorption range toward lower photon energies. This behavior is consistent with the modification of the ZnO electronic structure by Co-related states and defect-induced states within or near the band gap, as reported for Co-incorporated ZnO systems. In particular, the interaction between localized Co 3d states and the ZnO electronic states can modify the band structure and contribute to the observed band-gap reduction. Regarding the electrical response, Co incorporation results in a wider separation between the high-resistance and low-resistance states compared with undoped ZnO. Furthermore, although both films exhibit thermally activated transport in the high-temperature regime, the activation energy increases markedly from 44.7 meV for ZnO to 242.91 meV for ZnO:Co. This increase indicates that Co incorporation also modifies the

energetic landscape governing carrier transport, which may involve Co-related impurity states, defect complexes, and changes in grain-boundary barriers. Therefore, the simultaneous reduction in optical band gap and increase in transport activation energy suggest that Co incorporation modifies both the electronic structure and the defect-mediated transport processes in the ZnO matrix.

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