

Research Article

CuO/ZnO Bi-layered nanoarchitecture for room temperature CO₂ sensing at low concentrations

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ABSTRACT

Bi-layered ZnO/CuO nanostructured films have been examined for CO₂ gas sensing applications. X-ray diffraction, Fourier transform infrared, and Raman spectroscopy confirm the formation of a hexagonal wurtzite ZnO and a monoclinic CuO. Scanning electron and atomic force microscopies' observations reveal homogeneous, dense, and quasi-porous surfaces with smooth spherical sponge-like (ZnO), rough spherical-like (CuO and ZnO/CuO), and rough flat plate-like (for CuO/ZnO) grains morphologies with a few cracks. UV–visible spectroscopy shows greater transmittance (45–90 %) in the infrared and visible domains, while the energy bandgap decreases significantly from 3.3 eV for ZnO to 1.5 eV for the remaining films. The measurements of the sensor's electrical characteristics at room temperature, including current-voltage (I–V), sensitivity-concentration (S–C), and current-time (I–t), indicate a sensitivity to the presence of CO₂ gas and that the fabricated sensor exhibits excellent sensitivity and faster response/recovery times. Indeed, the ZnO thin-film sensor recorded the highest sensitivity of 44.77 % at 31 ppm carbon dioxide concentration at room temperature. Based on the results obtained, a sensing mechanism is proposed. The findings demonstrate that metal oxide multilayered nanostructures are promising candidates for applications such as gas sensing, photocatalysis, and UV photodetection.

1. Introduction

In April 2024, monthly average atmospheric carbon dioxide (CO₂) levels peaked at a record of 427 parts per million (ppm), which is an increase of about 3 parts per million compared to that of 2023 [1]. CO₂ has served various purposes, both in nature and for humans, such as in the chemical industry, medicines, carbonated beverages, fire extinguishers, wastewater treatment, food packaging, photosynthesis, and pneumatic applications [2]. However, this greenhouse gas, among other gases, contributes significantly to the global warming and climate change [3]. It was reported that greenhouse gases, like CO₂, absorb the infrared radiation (heat) emitted in the atmosphere; consequently, CO₂ molecules will vibrate and emit heat, which contribute to the rise in

ambient temperature [4]. The continuous rise in the concentration of CO₂ significantly contributed to ocean acidification, decalcification of marine organisms as well as causing storms, droughts, and wildfires [5, 6]. CO₂ can also cause negative health effects on humans. It was also reported that to exposure of human to certain levels of CO₂ results in breathing difficulties, headaches, dizziness, loss of consciousness, and in some severe cases to death [2]. Its effect on human health was found to be dependent on its concentration in the atmosphere and the duration of exposure to it such as (i) 3.3–5.4 % for 15 min breathing difficulties; (ii) 7.5 % for 15 min involves several symptoms like breathlessness, tachycardia, dizziness, and sweating; (iii); and death when the concentration of CO₂ is above 20 % [4]. Consequently, this requires urgent needs for the design and fabrication of affordable, responsive, and

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efficient CO₂ gas sensors.

Different types of CO₂ sensors have been developed since the 1980s, such as solid-state electrolyte and electrochemical sensors, Severinghaus electrodes, infrared, capacitive, resistive, surface acoustic waves, oxide semiconductor, optical, and electrochemical sensors [3,7,8]. Nevertheless, these gas sensors possess some drawbacks including the need for external power supply, high power consumption, high working temperature, and long detection time. Thus, such a type of gas sensor does not fulfill the long self-autonomy with lower power consumption and high detection sensitivity [8].

Recently, semiconducting metal oxide (SMOs) thin films have been utilized for gas sensing due to their easy synthesis and unique physicochemical properties. It was found that such a type of gas sensor is greatly influenced by grain morphology, surface area, surface topography, roughness, and porosity. This is because detection mechanisms in gas sensors depend on changes in electrical conductivity resulting from interactions with target gas molecules [9]. Numerous SMOs like ZnO, TiO₂, WO₃, SnO₂, CuO, and In₂O₃ were thoroughly investigated for gas sensing, thanks to their intrinsic properties to adsorb gas molecules and catalyze reactions [10].

Due to their interesting properties and abundance, Zinc (ZnO) and copper (CuO) oxides are extensively studied in the literature for diverse applications. As an n-type semiconductor, ZnO has a wide direct energy bandgap (3.3 eV at 300 K), a large exciton binding energy (60 meV) [11], and the charge carriers are electrons. This is due to the presence of intrinsic oxygen deficiency associated with Zn-interstitial or O₂-vacancy [12]. Whereas as a p-type semiconductor caused by an excess of oxygen, CuO has a direct energy bandgap (1.4 eV), higher hole mobility, and theoretical specific capacity [9,13]. Besides, the combination of two semiconductors was reported to effectively improve surface, optical, electrochemical, and gas sensing properties [2]. Furthermore, it is important to highlight that the combination of the two semiconductors ZnO and CuO forms an n-p heterojunction, favoring the existence of electron donor-acceptor pairs observed between n-type metal oxide and p-type metal oxide [14], and the immiscibility of these two materials. This will improve field emissions within the devices while also increasing charge carrier separation, thereby offering diverse potential technological applications in environmental sensing, photovoltaic energy conversion systems, optoelectronic devices, photocatalytic systems, gas sensing technologies, and solid-state energy storage platforms.

Christopher S. Dandeneau et al. designed a p-CuO/n-ZnO chemical sensor by investigating two configurations ZnO/CuO and CuO/ZnO thin film heterostructures. The I-V curves revealed that CuO/ZnO exhibited an enhanced sensing response to H₂ gas [15], since the CuO top layer possesses a high porosity compared to ZnO in ZnO/CuO sensor. Neha Batra et al. [16] developed an enzymatic biosensor fabricated from ZnO/CuO composite for fast and reliable detection of free/total cholesterol. In a recent study, Elmira Velayi et al. fabricated ZnO/CuO nanocomposite with fluorine-free surfaces exhibiting excellent superhydrophobic properties and reversible/stable wettability switching characteristics, as well as fast responses to external stimuli [17]. Another study, conducted by Ashok CH et al., reported that ZnO/CuO nanocomposite annealed at 800 °C, tested as a humidity sensor, exhibited high sensitivity and good response/recovery times [18].

For CO₂ gas sensing, composite and bi-layered thin films of ZnO and CuO were investigated. Abul Monsur Mohammed Musa et al. examined the sensing properties of ZnO/CuO films with varying molar ratios (0.3, 0.5, and 0.7) at room temperature and 10,000 ppm CO₂. It was found that the 0.7 M ratio sensor with porous thick layer (318 ± 5 nm) exhibited the best performance including higher sensing response of 48 % and response (~3 min)/recovery (~11 min) times [2]. T. Bhowmick et al. reported another configuration CuO/ZnO with the top layer CuO having a porous nanostructure, exhibited a much enhanced response of 47 % for 2500 ppm CO₂ at 375 °C, compared to single layer of ZnO and CuO; i.e. only 15 % at 300 °C and 16 % at 350 °C, respectively [7]. The sensor manifested selectivity towards CO₂ compared to CO and CH₄.

Christopher S. Dandeneau et al. incorporated ZnO and CuO thin films pre-deposited under optimized pyrolysis conditions, into alternating planar heterostructures ZnO/CuO and CuO/ZnO. The I-V measurements indicated that the sensor CuO/ZnO response was enhanced, at 4000 ppm of H₂ pyrolyzed at 250 °C [15].

This study aims to fabricate a CO₂ gas sensor based on bi-layered ZnO/CuO and CuO/ZnO films using a sol-gel dip-coating method. Despite its disadvantages such as aging of the sol, production of inhomogeneous layers at the borders of the substrate, predominantly on small-size supports, and fracture in thin films, especially for coatings on anisotropic crystals [19]. The advantages of this method include the ability to dip the substrate into the solution and pull it out at a constant speed, which provides good control over thickness, produces no waste, and is low-cost and effective [20], making it a reliable and efficient technique for the fabrication thin films.

The films were characterized and subsequently subjected to room temperature gas sensing measurements conducted in the voltage interval from -1.5 V to +1.5 V. The electrochemical characteristics were correlated with grain morphology and surface topography as well as the physicochemical characteristics of the fabricated thin films.

2. Experimental part

2.1. Materials synthesis

Solutions of ZnO and CuO were prepared by sol-gel method and ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films were deposited by HOLMARC apparatus (Model No. HO-TH-02B) onto pre-cleaned glass substrates. The cleaning was performed using successively acetone, methanol, ethanol, and deionized water. For the preparation of 0.4 M of ZnO and 0.4 M of CuO solutions, Zn acetate dihydrate [Zn(CH₃COO)₂·2H₂O] and Cu acetate monohydrate [Cu(CH₃COO)H₂O] were used as precursors, isopropanol (IPA) [C₃H₇OH], diethanolamine (DEA) [C₄H₁₁NO₂], and ethylene glycol (EG) [C₂H₆O₂] as solvent, stabilizer, and coating material, respectively. A homogeneous solution mixture was obtained by stirring at 60 °C for 2 h by a magnetic stirrer. The sol was matured for 1 day at room temperature under atmospheric pressure and then deposited onto 38 × 25 mm glass plates (SAIL BRAND, CAT. NO. 7101, China) by immersion.

The deposition conditions were optimized from our previous work as follows: 4 mm/s withdrawal speed, each deposited layer was subjected to drying for 5 min only at 400 °C, then the films were annealed in oven under open air at 500 °C for 1 h (Fig. 1a).

2.2. Materials characterization

X-ray diffraction (XRD) patterns were recorded in the range 20°–80° and a scan rate of 3°/min using a Philips X'Pert diffractometer equipped with Cu-Kα radiation source (λ = 1.5418 Å). Chemical bonds and functional groups were identified by recording Fourier transformed infrared (FTIR) patterns in the range 400–4000 cm⁻¹ at a resolution of 8 cm⁻¹ using a Thermo Nicolet (Nexus) apparatus. Molecular composition and structure were analyzed at 532 nm wavelength (green Laser) using a RENISHAW inVia Raman Microscope. Morphological observations were performed by scanning electron microscopy (SEM) using a Thermo Fisher Apero 2C model operating at 20 kV. The surface topography and roughness were characterized by atomic force microscopy (AFM) using MFP3D Asylum Research Oxford Instruments. The optical transmittance was measured in the range 190–1800 nm using a PerkinElmer UV-Vis-NIR Lambda 19 spectrophotometer.

2.3. Gas sensing measurements

The CO₂ gas sensing characteristics were performed at room temperature by monitoring the change of the electrical current while varying the gas concentration. This system measures the current using

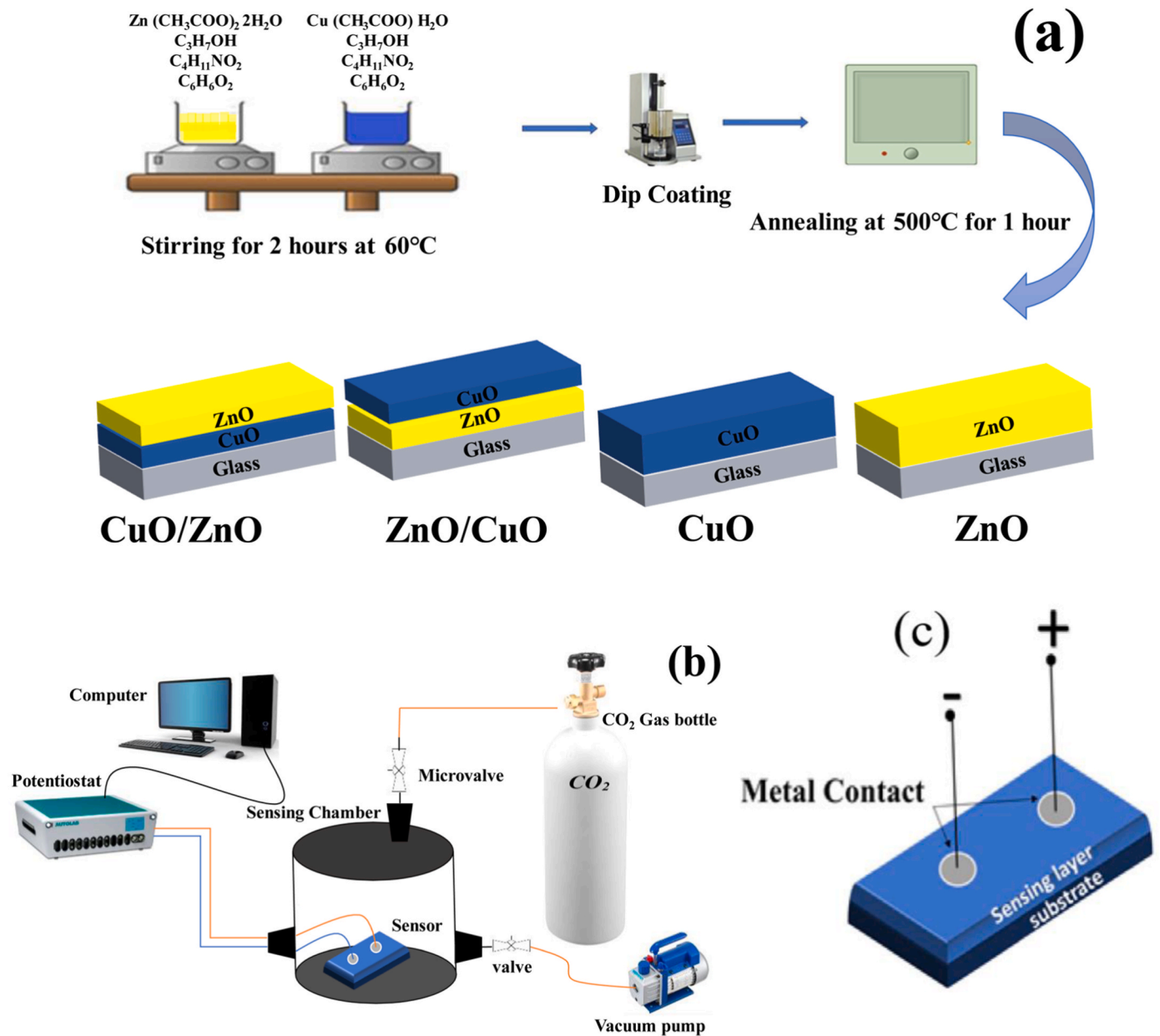


Fig. 1. (a) Schematic diagram for the synthesis and preparation of ZnO, CuO, ZnO/CuO, CuO/ZnO thin films, (b) Experimental setup for the CO₂ gas sensing, (c) Schematic of the planar gas sensor device with its two parallel metallic contacts deposited on the sensitive layer.

(Al) Ohmic metallic contact electrodes achieved by the deposition of 99.99 % pure Al, from a computer-controlled (programmable scanning) Potentiostat/Galvanostat used as source of power supply (Princeton Applied Research EG&G 362 Model) placed on top of the samples (coplanar contact), see Fig. 1(b–c).

The experimental setup involves positioning the samples within a gas chamber equipped with a detector probe to measure the gas pressure, and gas valves were used to inject gas into the chamber, as illustrated in Fig. 1b. Prior to CO₂ gas introduction, the chamber was vacuumed using a rotary pump. The gas sensitivity (*S* in %) was quantitatively determined as follow [10]:

$$S(\%) = \frac{(I - I_0)}{I_0} \times 100 \quad (1)$$

where *I*₀ and *I* represent the currents of the films measured in vacuum and at different gas concentrations, respectively.

2.4. Fabrication of the sensing structure

For CO₂ sensing, a planar device structure was adopted, since it is the most attractive and commonly used in literature, because of its simple design and low cost, see Fig. 1c. It is composed of two elements, a gas-sensitive semiconducting layer and Al electrodes (metal contacts) deposited on the same surface. These electrodes act only as collectors of carriers generated during the gas detection process; they are passive and do not contribute to gas detection.

For measurements, a DC maximum voltage of +1.5 V was applied to Al electrodes and the current flowing through the device was measured before (*I*₀) and after (*I*_{gas}) gas injection. The device's current can be expressed as a function of the change in resistance between these two electrodes. The electrical connection is established from these electrodes using conductive paste.

3. Results and discussion

3.1. XRD, Raman, and FT-IR analyses

3.1.1. XRD analysis

From the XRD patterns of ZnO, CuO, ZnO/CuO, and CuO/ZnO thin films displayed in Fig. 2a, pronounced and relatively broad diffraction peaks are observed, reflecting the formation of polycrystalline films.

For the ZnO film, the seven peaks located at 2θ of 31.85° , 34.55° , 36.35° , 47.69° , 56.75° , 63.09° , and 68.16° are indexed as (100), (002), (101), (102), (110), (103), and (112) reflections belonging to the hexagonal wurtzite-type structure of ZnO compound, as confirmed by the JCPDS card No. 01-079-0205. Besides, according to the peaks' relative intensity, it can be affirmed that ZnO film exhibits grain orientation preferentially along the (101) plane.

For the CuO film, the nine peaks located at 2θ of 32.63° , 35.66° , 38.85° , 48.95° , 53.61° , 58.54° , 61.73° , 65.98° , 66.59° , 68.36° , 72.78° , and 75.53° are indexed as (110), (-111) , (111), (-202) , (020), (202), (-113) , (022), (-311) , (220), (311) and (-222) reflections, characteristics of the monoclinic phase of CuO compound, in agreement with the JCPDS card No. 03-065-2309.

Surprisingly, for the ZnO/CuO film, the observed peaks correspond only to CuO phase, whereas no peaks belonging to ZnO phase can be detected. This may indicate that the thickness of the CuO layer is greater than that of the ZnO layer. Interestingly, for the film's CuO/ZnO XRD pattern, both ZnO and CuO peaks are observed.

The lattice parameters (a , b , c) of ZnO-hexagonal and CuO-monoclinic structures are computed using the following equations, in addition to the Bragg law [21]:

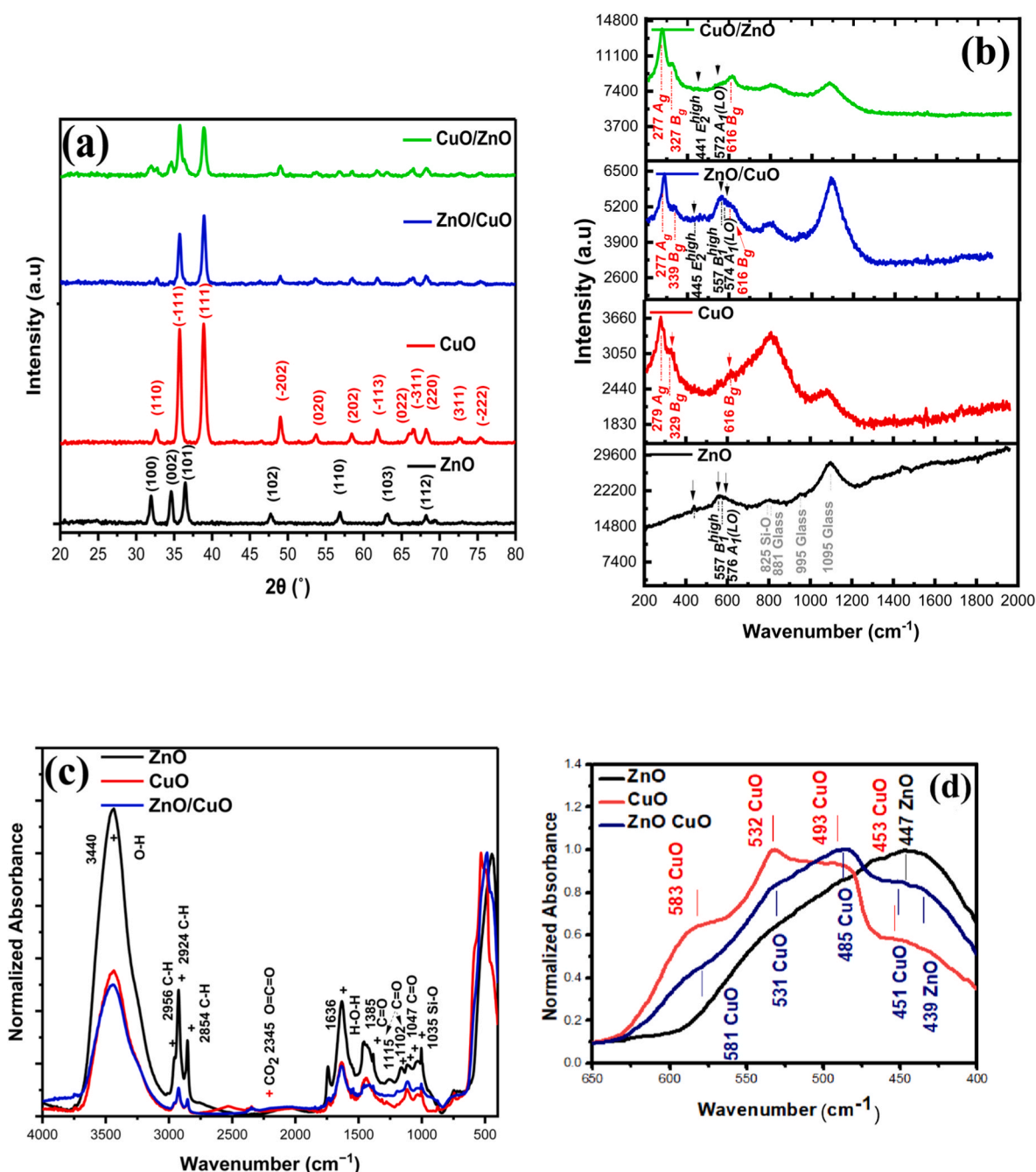


Fig. 2. (a) XRD patterns, (b) Raman and (c) FTIR spectra of ZnO, CuO, ZnO/CuO, and CuO/ZnO films, (d) zoom of FTIR spectra in the range 650 – 400 cm^{-1} .

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (2)$$

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \quad (3)$$

$$\lambda = 2d_{hkl} \times \sin \theta_{hkl} \quad (4)$$

where β is the angle of the monoclinic phase (α and γ are 90°), λ is the X-ray wavelength (1.5418 Å), θ_{hkl} the diffraction angle, and d_{hkl} is the interplanar distance.

The lattice parameters are found to be $a = b = 2.84$ Å and $c = 4.92$ Å for ZnO phase. For the CuO, ZnO/CuO and CuO/ZnO films, the lattice parameters are found to be very close, $a = 4.62$ Å, $b = 3.4$ Å, and $c = 4.3$ Å.

The mean crystallite size (D) can be computed from peak broadening by employing Scherrer's equation [22]:

$$D = \frac{0.94 \lambda}{\beta_{(hkl)} \times \cos \theta_{(hkl)}} \quad (5)$$

where β (in radian) is the full width at half maximum (FWHM).

The crystallite size estimated using the prominent reflections, (101) for ZnO and (111) for CuO are found at the nanometer scale and within the same range, i.e. ~ 16.7 nm for ZnO film; ~ 14.4 nm for CuO film; ~ 12.3 nm for ZnO/CuO film; and ~ 11.7 nm for CuO/ZnO film.

The microstrain (ϵ) [7] defined as the tiny deformations occurring within the film when subjected to stress and can be estimated from peak broadening, whereas the dislocation density (δ) [23] represents the length of dislocation lines per unit volume:

$$\epsilon = \frac{\beta}{4 \times \tan \theta} \quad (6)$$

$$\delta = \frac{1}{D^2} \quad (7)$$

From Table 1, it can be noted that the values of the microstrain are negative irrespective of the film, indicating a compressive strain that develops at the film/substrate interface describing crystal imperfection and distortion which may be associated with the difference of the lattice parameters between the deposited layer and the amorphous glass. Nevertheless, the value of the microstrain is found to be smaller for ZnO, CuO, and ZnO/CuO films within the range 0.06–0.18 % then increases markedly up to -1.37 % for CuO/ZnO. This can be attributed to the size effect, since small atoms increase the surface microstrain while large atoms decrease it [24]. The variation of the residual strain across the whole film can also be associated with several parameters, such as phase stabilization, difference between thermal expansion coefficients of the deposited layer and substrate, lattice mismatch between the oxide film and the substrate [24], and at the interface in bi-layered films [25]. Indeed, the evolution of microstrain in addition out-of-plane and in-plane strains in multilayered thin films is more complex and remains unclear.

For the dislocation density, the value is found to increase gradually, CuO higher than ZnO, and CuO/ZnO higher than ZnO/CuO. This may be due to the type of crystal structure as well as the mechanisms associated with the development and propagation of dislocations within each

crystal lattice. Indeed, it was reported that in the monoclinic crystal lattice of CuO, the dislocations develop faster compared to the hexagonal crystal lattice of ZnO. Furthermore, the reduction in particle size results in an increase in surface atom that is an energetic surface and therefore an increase in dislocation density [23,26] (according to Table 1) and an increase in defects levels and grain boundaries. In addition, the number of dislocations in the ZnO/CuO ($0.67 \times 10^{-2} \text{ nm}^{-2}$) and CuO/ZnO ($0.74 \times 10^{-2} \text{ nm}^{-2}$) bi-layered films rises, comparatively to pure ZnO ($0.35 \times 10^{-2} \text{ nm}^{-2}$) and CuO ($0.48 \times 10^{-2} \text{ nm}^{-2}$) oxides, as a result of the stress at the interface between the two layers [25]. It is important to note that the crystallinity, which describes the level of long-range structural order in a material [26], is better for pure ZnO than CuO, ZnO/CuO, and CuO/ZnO films. This is due to the inverse correlation between the dislocation density and crystallinity [26]. Indeed, ZnO has the smallest dislocation density value ($0.35 \times 10^{-2} \text{ nm}^{-2}$) among the synthesized films indicating its high degree of crystallinity. As the crystallinity is correlated with the film properties, this leads to an improvement of ZnO gas sensing characteristics.

3.1.2. Raman analysis

Nanostructure defects and structural disorder occurring during crystallization affect Raman scattering. Raman spectroscopy reflects the structural fingerprint of any substance and helps to identify the vibrational bands of functional species. It is known that ZnO crystallizes in a hexagonal wurtzite-type structure within the space group $P6_3mc$ (symmetry C_{6v}) and is composed of 2 formula units per primitive cell [27]. Theoretically, optical phonons have six symmetries divided into active and inactive modes. The five Raman active modes are: A_1 (TO); A_1 (LO), E_1 (TO), E_1 (LO), E_2^{high} , and E_2^{low} . Whereas only two B_1 (low) and B_1 (high) inactive modes are present and are normally silent [27–29]. Furthermore, it is common that A_1 and E_1 polar modes split into two modes, transverse (TO) and longitudinal (LO) optical phonons (also infrared active) [30]. CuO crystallizes in a monoclinic structure within the space group $C2/c$ (symmetry C_{2h}), and is composed of four formula units per primitive cell [31]. It contains twelve optical phonon modes distributed as follows: $\Gamma_{\text{RA}} = 4A_u + 5B_u + A_g + 2B_g$ [32]. The three Raman scattering modes are A_g , $B_g^{(1)}$, and $B_g^{(2)}$ [33]. The remaining nine infrared modes are subdivided into six active ($3A_u + 3B_u$) and three acoustic ($A_u + 2B_u$) [34].

In this investigation, the Raman spectra of ZnO, CuO, ZnO/CuO, and CuO/ZnO films are depicted in Fig. 2b. In the ZnO Raman spectrum, the three peaks at 440, 557, and 576 cm^{-1} corresponds to the E_2^{high} , B_1 (high), and A_1 (LO) modes of ZnO, respectively and are closed to the reported data.^{25 26} ZnO crystallinity is influenced and weakened by the deposition of ZnO/CuO bi-layered films and altering the ZnO and CuO oxide phases. The peak observed at 576 cm^{-1} is assigned to A_1 (LO) first-order phonon peak [35], reflects the high crystalline quality of the grown ZnO film. It was reported that E_2 and A_1 (LO) are the only allowed modes for backscattering along the preferred c -axis of the crystal [29]. For higher crystalline ZnO phase, the A_1 (LO) band was found to be the strongest among all bands [27]. The Raman non-active or silent modes, like the first-ordered B_1 (high), became activated by introducing defects [36]. It is worth mentioning that the silent Raman modes have been studied theoretically [37,38] and experimentally [36]. The observed band located at 557 cm^{-1} in ZnO film is ascribed to B_1 (high) silent mode,

Table 1
Structural and microstructural parameters of ZnO, CuO, ZnO/CuO, and CuO/ZnO films.

Films	Phase	Plane (hkl)	2θ ($^\circ$)	FWHM β ($^\circ$)	D (nm)	Microstrain ϵ (%)	$\delta \times 10^{-2}$ (nm^{-2})	Lattice Parameters (Å)
ZnO	ZnO	(101)	36.46	0.522	16.73	−0.18	0.35	$a = 2.841$; $b = 4.923$
CuO	CuO	(111)	38.90	0.56	14.43	−0.07	0.48	$a = 4.620$; $b = 3.421$; $c = 4.343$
ZnO/CuO	CuO	(111)	38.90	0.51	12.27	−0.06	0.67	$a = 4.623$; $b = 3.441$; $c = 4.333$
CuO/ZnO	CuO	(-111)	35.70	0.63	11.68	−1.37	0.74	$a = 4.621$; $b = 3.414$; $c = 4.326$

which corroborates with the calculated value (557 cm^{-1}) reported by Manjón et al. [37] Musa et al. [36], observed both active B_1 (low) and silent B_1 (high) Raman modes at 273 and 538 cm^{-1} , respectively while Chen et al. [39] reported that the B_1 (high) mode appears at slightly higher wavenumber $\sim 560\text{ cm}^{-1}$.

Herein, it can be concluded that the observed Raman modes and their respective positions in this study agree well with the reported experimental and theoretical values. Nevertheless, the Raman signal is very sensitive to the type of crystal structure and the structural and microstructural defects [40].

The main E_2^{high} phonon mode is a characteristic of ZnO wurtzite hexagonal phase and is usually ascribed to oxygen atoms lattice vibrations, thereby confirming its formation in agreement with XRD analysis. It was found that the broadening (expressed as the full width at half maximum - FWHM) and relative intensity of this band reflect the degree of crystallinity [41]. By comparing the relative E_2^{high} peak intensity (18552 cm^{-1}) of ZnO film and CuO/ZnO (7698 cm^{-1}) and ZnO/CuO (4645 cm^{-1}) films, the observed slight increase can be attributed to the reduction of the residual stress, thus resulting in higher crystalline quality of pure ZnO oxide film [39]. Also, the sharpness and low FWHM of E_2^{high} band for ZnO film suggest its improved crystallinity, which corroborates well with ZnO and CuO/ZnO XRD patterns.

Besides, the contribution of the glass substrate in the Raman spectrum of ZnO film (Fig. 2b), is reflected by the appearance of a high frequency halo with maxima at $\sim 825, 881, 995$ and 1095 cm^{-1} , in addition to a band located at $\sim 576\text{ cm}^{-1}$. This may be due to the utilization of a solid-state laser of 532 nm and/or the smaller thickness of ZnO layer. This is in agreement with the glass bands observed by Loiko et al. [42]. The substrate modes are superposed or overlaid on the A_1 and E_1 ZnO modes, which explains the difficulty of separating the frequency of these modes from the substrate [43].

The Raman spectrum of CuO film (Fig. 2b) illustrates three bands at $279, 329$, and 616 cm^{-1} assigned to $A_g, B_g^{(1)}$, and $B_g^{(2)}$ of CuO phase [44]. A shift to a lower wavenumber (blue shift) alongside broadening can be observed between film and bulk CuO frequencies, as summarized in Table 2, which is usually associated with quantum confinement of CuO nanostructures. However, no other bands referring to Cu_2O modes ($218, 109, 149$, and 630 cm^{-1}) can be detected, inferring that the as-grown CuO film is a single phase [45].

Interestingly, for both bi-layered CuO/ZnO and ZnO/CuO films, the corresponding spectra shows the presence of CuO as major phase, as manifested by the strong band [45] at $\sim 279\text{ cm}^{-1}$. Its relative intensity reflects the highly ordered and crystalline structures of CuO than ZnO oxides. However, the appearance of less intense bands at $\sim 441/\sim 445\text{ cm}^{-1}$ and $\sim 572/\sim 574\text{ cm}^{-1}$ for CuO/ZnO and ZnO/CuO, respectively signifies to the co-existence of ZnO phase with lesser crystallinity in both bi-layered films. Hence, both films are in fact biphasic containing CuO and ZnO phases, although the latter cannot be identified by Raman or by

XRD analyses. Comparing ZnO nanoparticles deposited without and with CuO nanoparticles, the E_2^{high} mode decreases in intensity and shifts more to the high frequencies with a broadening due to the existence of CuO phase in the bi-layered films. The CuO/ZnO film is characterized also by the disappearance of the B_1^{high} non-active Raman mode.

3.1.3. FT-IR analysis

Fig. 2c depicts the FT-IR spectra of pure and bi-layered ZnO/CuO films to identify their specific vibration modes at room temperature and Fig. 2d illustrates a zoom in the range $650 - 400\text{ cm}^{-1}$. The FT-IR spectra confirm the high purity of the deposited films. The FT-IR spectrum of ZnO film consists of a principal strong band at $\sim 447\text{ cm}^{-1}$ assigned to Zn-O characteristic stretching vibrations bond [46] and blue shifted compared to its value of $\sim 437\text{ cm}^{-1}$ of its bulk counterpart, as previous studies [46–49] reported it approximately between 404 and 466 cm^{-1} .

The FT-IR spectrum of CuO film consists four bands at $\sim 453, \sim 493, \sim 532$, and $\sim 583\text{ cm}^{-1}$ ascribed to typical stretching vibrations of Cu-O bond in the monoclinic structure of CuO phase [47,50,51]. Consequently, confirming the formation of CuO phase. The IR active mode observed at $\sim 453\text{ cm}^{-1}$ corresponds to the high frequency A_u mode of CuO structure, as reported in the literature [51–53]. Whereas the bands at ~ 532 and $\sim 583\text{ cm}^{-1}$ ascribed to the B_u mode and the other B_u mode are characteristic of Cu(II)-O stretching vibrations in CuO [54]. Furthermore, the band at $\sim 493\text{ cm}^{-1}$ corresponds to Cu(II)-O stretching vibrations in CuO [55]. Besides, no additional bands in the range of $605\text{--}660\text{ cm}^{-1}$ can be detected, excluding the presence of any secondary phase such as Cu_2O [55] or other impurities.

After the deposition of ZnO/CuO bi-layered film, a broad and strong band appears at $\sim 500\text{ cm}^{-1}$ originating from both ZnO and CuO phases. This broadband is in fact the superposition of the main $\sim 439\text{ cm}^{-1}$ ZnO IR signature band (Zn-O) and the four CuO IR bands assigned to A_u (~ 451 and $\sim 485\text{ cm}^{-1}$), and B_u (~ 531 and $\sim 581\text{ cm}^{-1}$). Narang and al [56], have assigned the observed weaker band at 490 cm^{-1} as 344 cm^{-1} (B_g) + 147 cm^{-1} (B_u) combination bands. As seen in Fig. 2c, the IR bands shifted to lower frequencies for ZnO/CuO bi-layered film in comparison to pure ZnO and CuO films. This red shift may result from the lattice mismatch between CuO and ZnO, which affect the effective force constant and subsequently the strain [46].

Common bands in all-IR spectra are observed above $\sim 600\text{ cm}^{-1}$ frequency. The band at ~ 3440 and $\sim 1636\text{ cm}^{-1}$ correspond to the deformation modes of H-O stretching and bending in H-O-H vibration of adsorbed water, respectively [57]. Some residual organic groups such as C=O stretching mode of acetate [40] precursor salt is detected at $\sim 1385\text{ cm}^{-1}$. The absorption bands at $\sim 2854, \sim 2924$, and $\sim 2956\text{ cm}^{-1}$ are ascribed to the C-H stretching vibrations of alkane groups [48]. The band at $\sim 1035\text{ cm}^{-1}$ is due to the deformation vibrations of Si-O of the substrate. The weak band at $\sim 2345\text{ cm}^{-1}$ is attributed to CO_2 from atmosphere, since IR analysis is recorded in air [46]. The FT-IR analysis agrees well with XRD analysis, indicating the formation of ZnO and CuO oxides in the deposited films.

3.2. Surface morphology and topography observations

3.2.1. Field emission scanning microscopy (FESEM) analysis

The FESEM images of the grown films, as depicted in Fig. 3, reveal some differences in surface morphology and roughness. The ZnO film (Fig. 3a) appears to be significantly more homogeneous, smooth, and sponge-like porous structure, with very small grains uniformly distributed throughout the surface. In addition, a few cracks can be observed, most probably attributed to the stress induced by the drying of the layer. The quasi-spherical shaped particles exhibit a uniform size distribution at the nanometer level in the range $40\text{--}50\text{ nm}$ compared to other films [58]. This results in a higher surface area and thus better sensing performance [59]. It is well known that the sol-gel process dip-coating method produces a very dense and homogenous layer with nearly

Table 2

Theoretical and experimental (results of this work) frequencies (in cm^{-1}) of the Raman modes of single- and bi-layered ZnO and CuO [27,68,70].

Modes	ZnO ^{2d} , CuO ⁴³ (cm^{-1})	ZnO (cm^{-1})	CuO (cm^{-1})	CuO/ ZnO (cm^{-1})	ZnO/ CuO (cm^{-1})
ZnO					
E_2^{low}	101				
$A_1(\text{TO})$	380				
$E_1(\text{TO})$	407				
E_2^{high}	437	440		441	445
$A_1(\text{LO})$	574	576		572	574
$E_1(\text{LO})$	583				
$B_1^{\text{high}}(\text{silent})$	552 ⁴²	557			557
CuO					
A_g	296		279	277	277
$B_g^{(1)}$	344		329	327	339
$B_g^{(2)}$	629		616	616	616

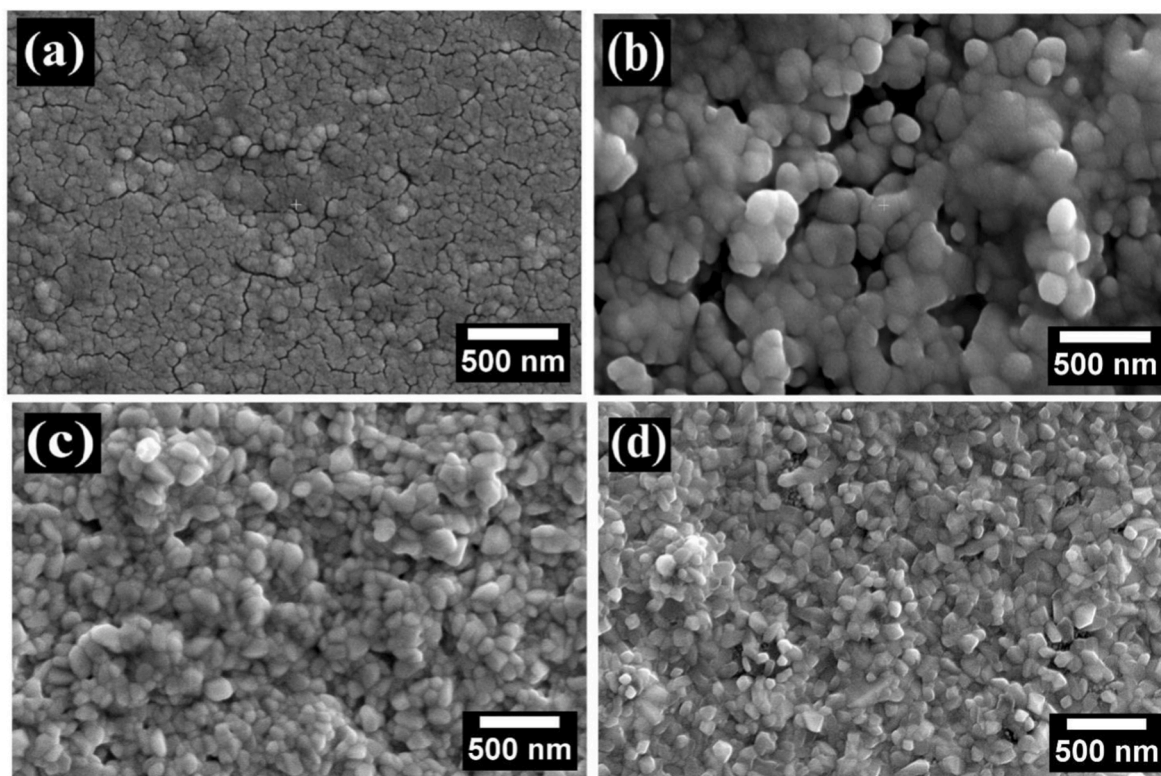


Fig. 3. FESEM images of (a) ZnO, (b) CuO, (c) ZnO/CuO, and (d) CuO/ZnO films.

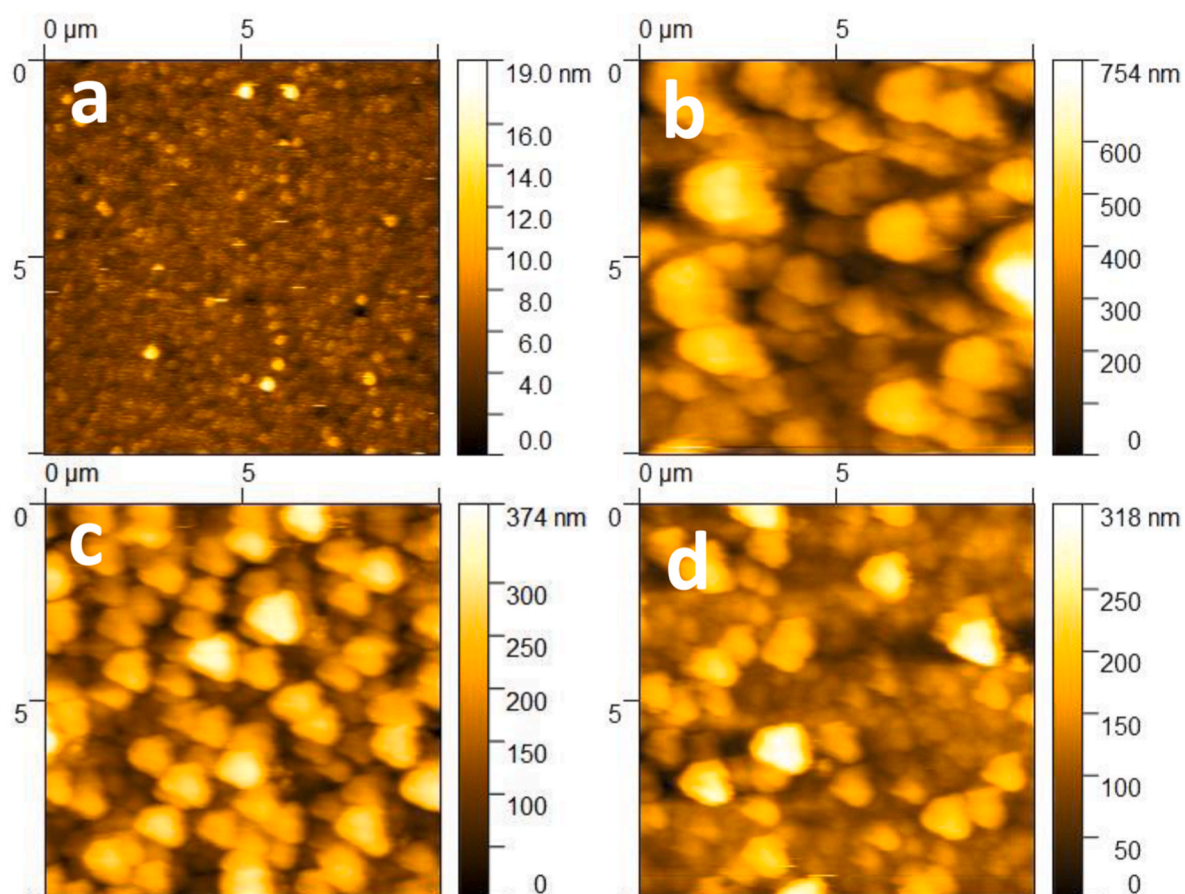


Fig. 4. AFM images of (a) ZnO, (b) CuO, (c) ZnO/CuO, and (d) CuO/ZnO films.

complete surface coverage when compared to alternative methods.

For CuO film (Fig. 3b), the particle size distribution is randomly, with the presence of both large (250 nm) and small (100 nm) with spherical-like shape, in concordance with morphology visualized in previous research [60].

For ZnO/CuO bi-layered film (Fig. 3c), the SEM image shows a relatively smaller spherical-like CuO grain size, as compared to that of the single-layered CuO film. Bhowmick et al. [7] reported similar morphological observations in the ZnO/CuO film deposited by dip-coating and attributed the grain size reduction primarily to the growth of CuO thin layer over well-crystallized ZnO grains.

Fig. 3d shows the morphology CuO/ZnO bi-layered film. Interestingly, it is observed that the grain morphology changes to a flat plate-like shape when the ZnO layer grows onto the under-layer CuO, compared to the quasi-spherical grains in the single-layered ZnO film (Fig. 3a). The grain size is obtained by ImageJ software, ZnO grain distribution is random (see inset) in the range 150–300 nm for CuO/ZnO film but is denser with smaller grain size distribution in the range 60–200 nm of ZnO/CuO film (Fig. 3c). This may be due to larger number of Cu nucleation centers [61].

The seed would, therefore, be divided and this would result in an increased number of grains of lower size. It is noteworthy that the morphology of films' surface shows the existence of porous regions giving an effective area for the reactive gas to react effectively, hence the sensitivity would be enhanced significantly.

3.2.2. Atomic force microscopy (AFM) analysis

The surface topography of the films was characterized using amplitude modulation AFM imaging in tapping mode (Fig. 4), and the surface roughness was computed with Gwyddion software [62] (Table 3). The ZnO film (Fig. 4a) presents a very smooth and homogenous surface in agreement with the literature [63], composed of small grains with homogeneous size distribution. Whereas CuO film (Fig. 4b) exhibits a very rough and non-homogeneous surface, composed of larger grains with a homogeneous size distribution. The surface roughness of ZnO is extremely small ~ 1 nm, which increases significantly for CuO reaching ~ 23 nm. Indeed, smaller grains form a continuous layer with negligible porosity (Fig. 4a), while larger grains form a discontinuous layer with a higher degree of porosity (Fig. 4b). This will influence the optical properties and gas sensing performance.

For the bi-layered CuO/ZnO and ZnO/CuO films, the surface topography seems to be affected by the order of layers. Indeed, ZnO/CuO film (Fig. 4c) is composed of grains that are larger than ZnO but smaller than CuO, whereas CuO/ZnO film (Fig. 4d) is composed of both small and large grains. Interestingly, both the porosity level and surface roughness of CuO/ZnO are smaller compared to ZnO/CuO, and the surface roughness is increased then reduced compared to ZnO and CuO films, respectively. The CuO and ZnO layers seem to strongly influence the roughness of ZnO and CuO top layers, respectively. Vuong et al. [64] reported that CuO changed the surface roughness of ZnO. Notable when the top layer is CuO, the surface roughness is greater than when the top layer is ZnO. The films display nanocrystals agglomeration in grains of different sizes on their surfaces with the existence of voids between these agglomerated grains. The AFM and SEM results are compatible in terms of surface topography for all films.

Table 3
Analysis of the roughness parameters R_a (the arithmetic average roughness) and R_{RMS} (the root-mean-square average roughness).

Films	R_a (nm)	R_{RMS} (nm)
ZnO	0.6	0.8
CuO	17.9	23
ZnO/CuO	17.6	21.3
CuO/ZnO	8.9	11.6

3.3. Optical properties

The spectral optical transmittance $T(\lambda)$ of the fabricated films is displayed in Fig. 5a. It is observed that ZnO film exhibits a high optical transmittance exceeding 90 % in the visible range (380–780 nm), while CuO film shows a much lower transmittance of 47 %. This can be correlated with the surface topography and roughness; indeed, ZnO film has a minimal surface roughness of ~ 1 nm, compared to the higher surface roughness of CuO of ~ 108 nm. For bi-layered ZnO/CuO and CuO/ZnO films, the optical transmittance seems not to be influenced by the order of layers, 38 % and 42 % at 800 nm, respectively.

The energy bandgap is estimated from the first derivative of the optical transmittance ($dT/d\lambda$), as shown in Fig. 5b, using the equation [65]:

$$E_g = \frac{hc}{\lambda_{max}} \quad (8)$$

where h represents the Planck constant, c the light velocity, and λ_{max} the wavelength at which the first derivative is maximum.

The calculated values of the energy bandgap are: 3.30, 1.58, 1.578, and 1.589 eV for ZnO, CuO, ZnO/CuO, and CuO/ZnO films, respectively. The computed direct bandgap energy of ZnO (3.3 eV) and the indirect bandgap energy of CuO (1.58 eV) agree well with the values reported in the literature [66]. It can be noticed that for ZnO/CuO and CuO/ZnO bi-layered films, the energy gap values are very close to the gap energy for CuO film. This could be due to the dominant influence of CuO's properties, as the band structure and properties of the individual oxides can interact in complex ways. Therefore, the resulting energy gap for ZnO/CuO or CuO/ZnO would often resemble that of CuO rather than that of ZnO due to the influence of the oxide with the narrower energy gap.

Fig. 5c illustrates evolution of the energy gap and stress vs. ZnO, CuO, ZnO/CuO, and CuO/ZnO films. It can be noted that the band gap has an inverse relationship with the microstrain. The latter refers to the small-scale deformation or distortion in a material's crystal lattice structure, which can affect the electronic and thus the physicochemical properties of the material, including its energy band gap. Indeed, in some cases, increased microstrain can lead to a narrowing of the band gap, making it easier for electrons to transition between energy bands. The inverse relationship observed in Fig. 5c may be due to various intrinsic and extrinsic factors. For example, increased microstrain may lead to changes in the atomic arrangement within the crystal lattice of the material (atomic positions and bond distances), altering its electronic structure and thus affecting the band gap. Understanding and controlling the relationship between microstrain and energy bandgap is critical for optimizing the performance of these films for gas sensors.

3.4. CO₂ gas sensing measurements

3.4.1. Current-voltage characteristics

Fig. 6 depicts the current-voltage (I–V) characteristics of the fabricated sensing devices based on ZnO, CuO, ZnO/CuO, and CuO/ZnO films measured at room temperature under the following operational conditions: (i) different atmosphere including vacuum, air, and in the presence of varying CO₂ gas concentrations (15.5–124 ppm), (ii) the potential ranges from -1.5 V to $+1.5$ V. It can be observed that within the range of the CO₂ concentrations used in this study, the current varies linearly with the potential and that the curves are symmetrical concerning the potential, suggesting a resistive behavior of the sensing devices. Moreover, as seen in Fig. 6, irrespective of the device structure, the I–V curves under CO₂ environment look similar to those recorded under air environment. When comparing the I–V curves upon exposure to air and CO₂, it can be observed that for a constant potential, the current varies with the rise in gas concentration, particularly for the ZnO-based sensor, where there is a perceptible rise in the current is

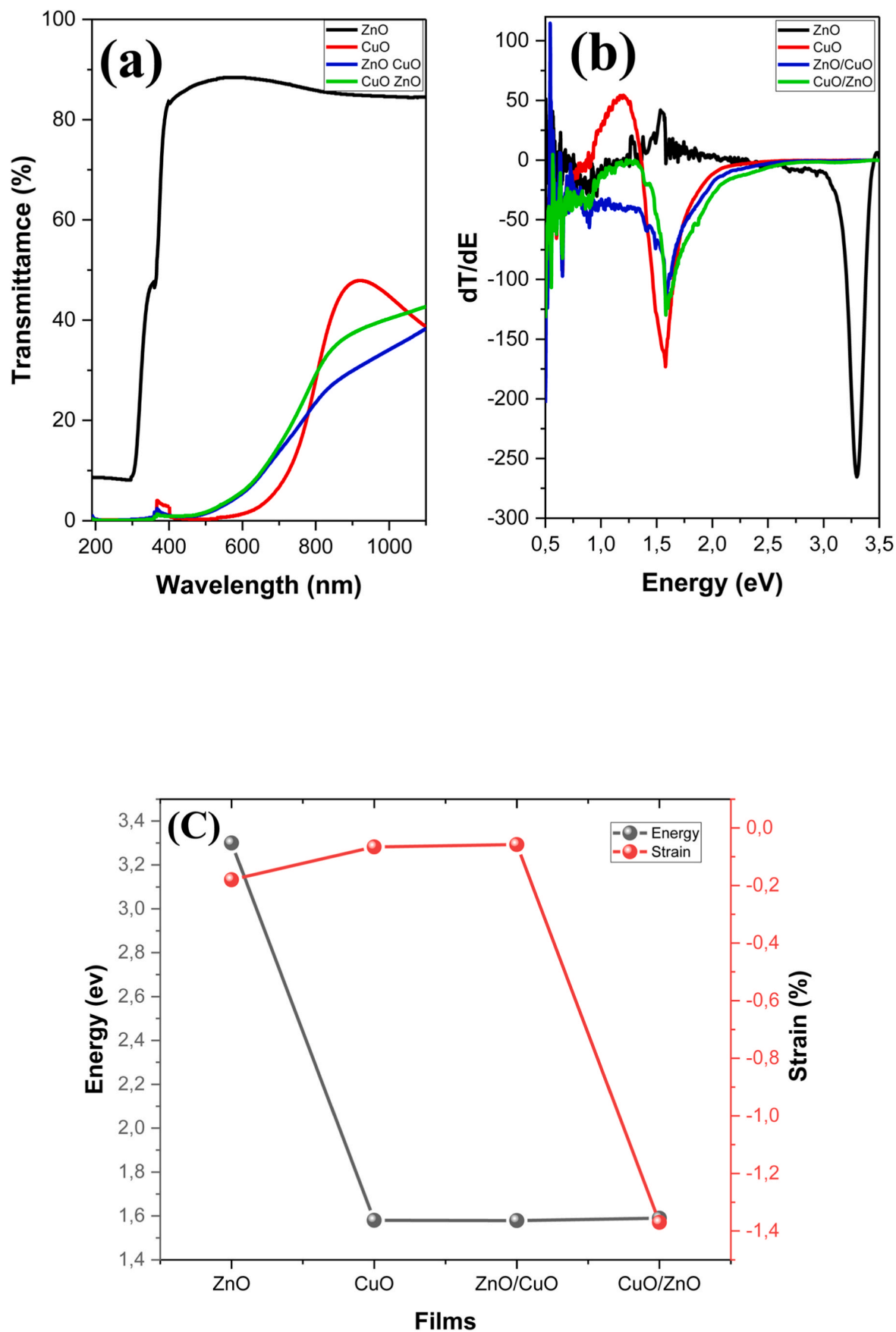


Fig. 5. (a) Transmittance spectrum, (b) First derivative ($dT/d\lambda$) plot of the transmittance spectra and energy bandgap vs. strain of ZnO, CuO, ZnO/CuO, and CuO/ZnO films.

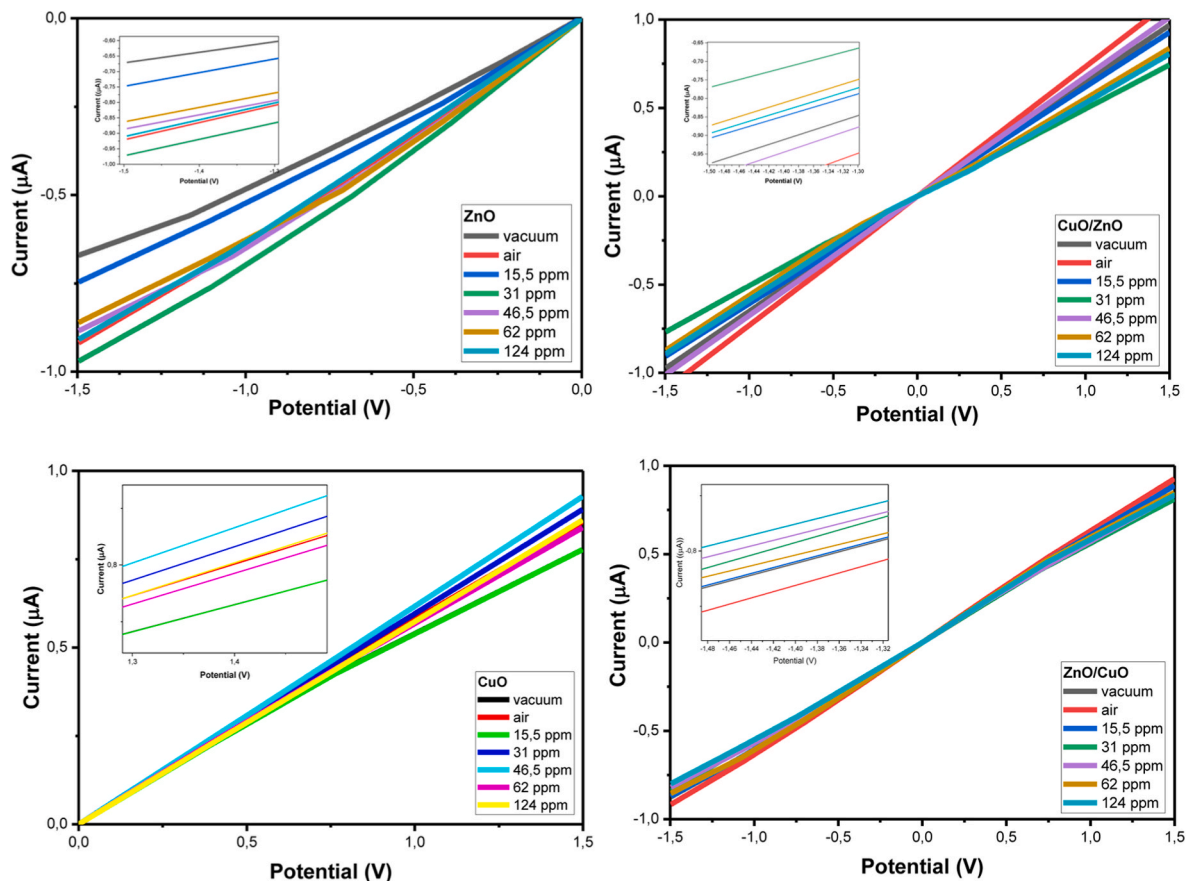


Fig. 6. I–V characteristics of ZnO, CuO, ZnO/CuO, CuO/ZnO sensors toward CO₂ gas at 25 °C and different concentrations.

observed with increasing gas concentration. This suggests that the sensitivity of the sensor structure depends primarily on the presence of CO₂, making it promising for further investigation.

Moreover, the zoom in the narrow potential range (–1.5) – (–1.3 V) shown in Fig. 6 indicates a noticeable increase in current due to CO₂ exposure, which highlights the sensor's sensitivity in this potential range.

3.4.2. Sensitivity-concentration dependence

Fig. 7a shows the variation of the sensitivity (defined as $S = \frac{I - I_0}{I_0}$) of the fabricated sensing devices as a function of CO₂ concentration at a constant bias potential and room temperature. It can be observed that for all studied structures, the sensitivity increases with the CO₂ concentrations reaching a maximum, then decreases and stabilizes. The maximum sensitivity of 44.77 % at a low concentration of 31 ppm is found for ZnO sensor. In contrast, the CuO sensor exhibits a lower sensitivity of about 20 % at 46.5 ppm, demonstrating better ZnO-based sensor performance compared to CuO. Regarding the bi-layered sensors, the CuO/ZnO exhibits a higher sensitivity (21 % at 31 ppm), compared to that of ZnO/CuO (6.5 % at 46.5 ppm), which corroborates with the previous observation when comparing single-layered ZnO and CuO sensors. The superior sensitivity of ZnO compared to CuO is primarily attributed to its higher electron mobility, wider band gap, greater surface reactivity, and larger specific surface area, all of which enhance gas adsorption and facilitate more efficient charge transfer during CO₂ detection.

While the typical ambient concentrations of CO₂ are about 400 ppm, the detection of concentrations as low as 31 ppm is relevant, for example, in sensor calibration, in some controlled lab environments, and in newer applications such as portable indoor air quality monitors or sensitive greenhouse control systems.

Our sensor showed stable sensitivity throughout the 31–124 ppm range, thus offering the potential for low-level detection with good accuracy. Such a feature will be highly useful in future scenarios where low CO₂ baselines either are created artificially or must be monitored for precision.

3.4.3. Response and recovery times

The response and recovery times of the fabricated sensors based on single-/bi-layered CuO and ZnO oxides vs. CO₂ concentration, have been determined graphically from the dynamic response of the sensors subjected to a varying CO₂ concentration. The time required by a sensor to reach 90 % of its final equilibrium output (baseline) following a measured input change represents the response time, whereas the time required for the sensor to return to 10 % of the baseline represents the recovery time [67]. Therefore, response/recovery times are equivalent to adsorption/desorption of CO₂. By measuring response/recovery times, the performance and reliability of a gas measurement system to changes in gas concentration can be evaluated.

Fig. 7b shows the dynamic response of the ZnO sensor at an applied voltage of 0.5 V for different CO₂ concentrations. It is noteworthy that after the gas is introduced into the chamber, the sensor's current increases gradually until it reaches saturation, then it returns to its initial value once the gas is turned off. These times correspond to CO₂ gas adsorption and desorption, respectively. Fig. 7 (c and d) depicts a typical example of response time (τ_{resp}) and recovery time (τ_{rec}) for ZnO thin film under 46.5 ppm CO₂. It can be noticed that the planar ZnO sensor exhibits fast response/recovery times of 13.5/9.8 s, respectively.

Fig. 8 depicts response/recovery times of the fabricated sensors acquired under varying CO₂ concentration. For the ZnO sensor (Fig. 8a), it is clearly seen that both response/recovery time decrease with increasing the CO₂ concentration, reaching minimum values at 62 ppm,

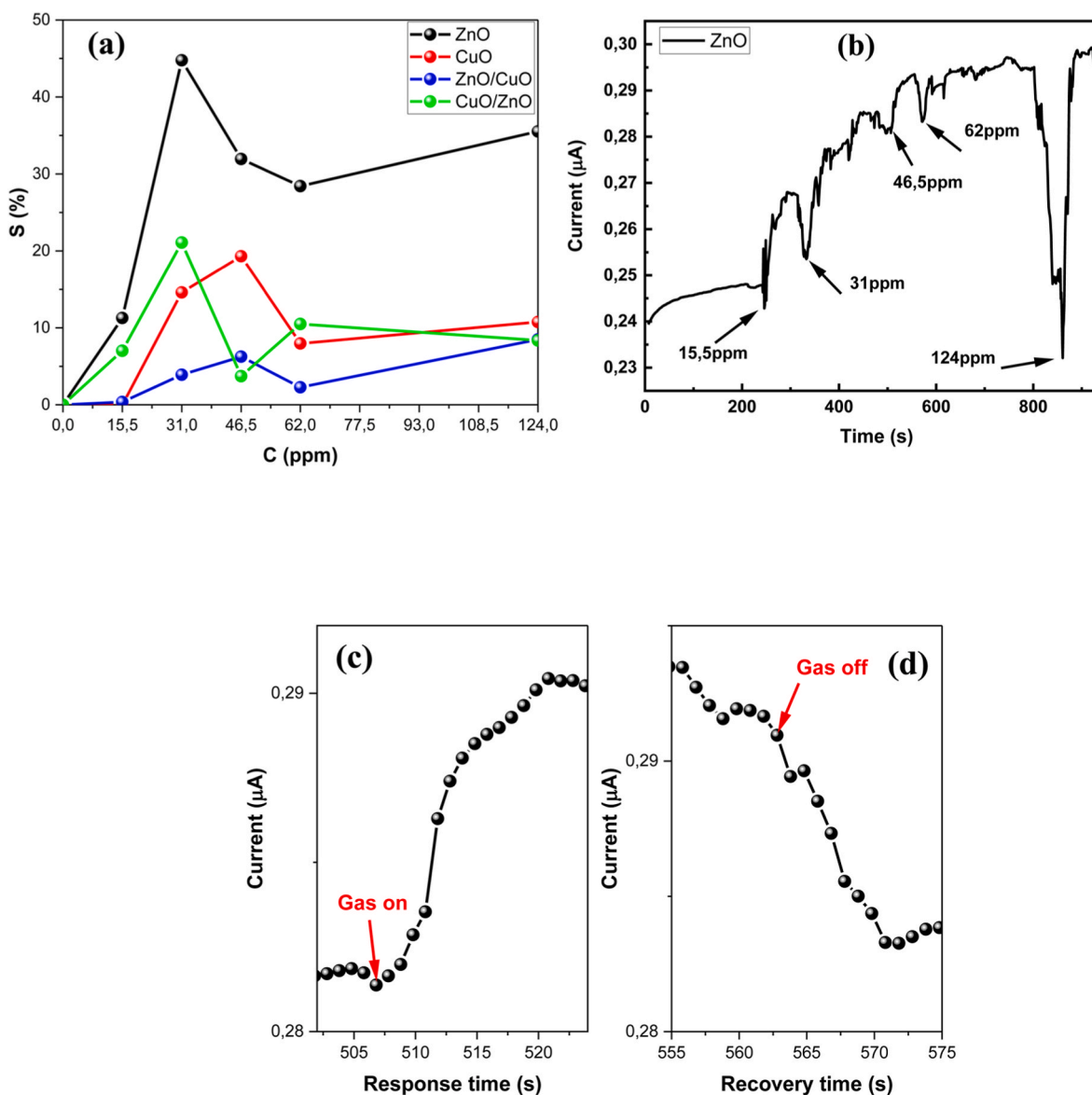


Fig. 7. (a) S–C sensitivity of the ZnO, CuO, ZnO/CuO, and CuO/ZnO sensor toward CO₂ gas at a temperature of 25 °C and different concentrations. Bias potential 0.5 V. (b) Dynamic response of ZnO in different CO₂ gas concentrations at 0.5 V applied bias, (c) Response -time and (d) Recovery-time measurement of ZnO thin film for 46.5 ppm CO₂ concentration.

then increase for higher CO₂ concentrations. This common phenomenon reported in literature is attributed to the saturation of the sensor surface. For the CuO sensor (Fig. 8b), the same phenomenon is observed as for ZnO sensor, a decrease in response and recovery times up to the minimum 62 ppm, however, a stabilization in (τ_{rep}) and (τ_{rec}) times is reached for higher CO₂ concentrations. One can observe that both ZnO and CuO sensors exhibit short response time (10.79 s for ZnO and 18.97 s for CuO) and very fast recovery time (9.0 s for ZnO and 8.1 s for CuO).

The response/recovery times of the bi-layered sensors as a function of CO₂ concentration behave differently depending on the top layer, either CuO or ZnO. Indeed, for the ZnO/CuO sensor (Fig. 8c), the response/recovery times increase until reaching maximum values at a concentration of 31 ppm, decrease sharply till 62 ppm, then followed by a gradual decrease for higher CO₂ concentrations. However, for the CuO/ZnO sensor (Fig. 8d), the first minimal decrease of both response/recovery times is attained at 31 ppm, and then both increase slightly. The above observations evidenced the effect of the type (intrinsic) and characteristics (extrinsic) of the material in contact with the tested gas.

3.5. Comparison with literature

The sensing characteristic towards CO₂ for single-layered ZnO and CuO and bi-layered ZnO/CuO and CuO/ZnO obtained in this study are compared to similar sensors reported in literature, see Table 4. It is clearly seen that the fabricated ZnO sensor demonstrates a better performance in terms of sensitivity and response/recovery times compared to similar sensors reported by several authors, specifically at higher temperatures above 250 °C and concentrations higher than 200 ppm.

For example, Kannan et al. [68], deposited nanostructured ZnO thin films onto glass substrates by DC reactive magnetron sputtering and tested for CO₂ sensing, but achieved a lower sensitivity of 10 % for 200 ppm at 300 °C and response/recovery times of (10–20 s)/(20–50 s), respectively which are much lower by 4 times compared to the fabricated ZnO sensor with a sensitivity of 44 %. Recently, S. Kanaparthi et al. [69] synthesized ZnO nanoflakes (NFs) by low-temperature precipitation method, exhibiting a high sensitivity of 22.5 % with faster response/recovery times (9/17 s) to CO₂ gas. This relatively high sensitivity was attributed primarily to the large surface-to-volume ratio

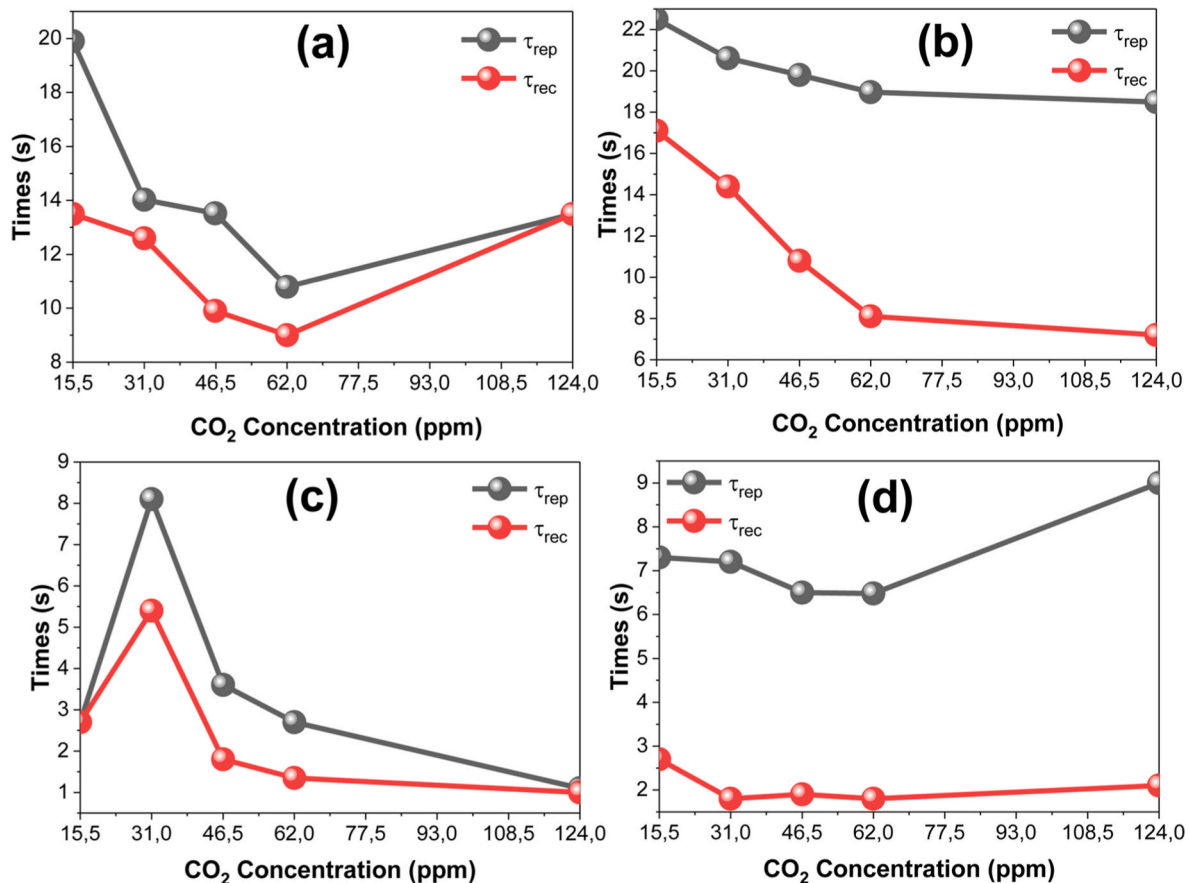


Fig. 8. Dynamic response (τ_{rep}) and (τ_{rec}) vs. CO_2 concentration of (a) ZnO, (b) CuO, (c) ZnO/CuO, and (d) CuO/ZnO films at bias of 0.5 V and room temperature.

Table 4

Comprehension comparison of CO_2 sensing performance with literature.

Sensor Materials	Synthesis Method	Morphology	Temperature ($^{\circ}C$)	Response (%)	$(\tau_{rep})/(\tau_{rec})$ (s)	Concentration (ppm)	Reference
ZnO	DC Magnetron Sputtering	Thin Film	300	10	10-20/20-50	2000	[66]
ZnO	Precipitation	NFs	250	22.5	9-17	200-1025	[67]
ZnO	Sol/Gel	Thin Film	300	11	20/20	1000	[76]
Ca-ZnO	Chemical Synthesis	Thin Film	350	53	135/180	50000	[42]
Au-ZnO	VLS Technique	1-D Nanostructure	250	80	70/60	200	[69]
CuO	Sol/Gel	Thin Film	300/250	21/10	5/5	8354	[71]
CuO	Thermal Evaporation	Thin Film	Room T°	14	320/230	500 mbar	[72]
CuO	Spray Pyrolysis	Thick Film	Room T°	3.5	10/6	100	[73]
CuO	Thermal Evaporation	Nanowires	400	101	15/35	1.05	[74]
CuO/ZnO	Chemical Deposition	Bi-layer Thin Film	375	47	44/217	2500	[7]
CuO/ZnO	Dip Coating	Thin Film	Room T°	48	180/660	10000	[2]
CuO/ZnO	Mechanical	Pellets	300	30	—	1000	[75]
ZnO	Sol-gel dip-coating	Thin films	Room T°	44.7	14.0/12.6	31	This work
CuO				14.6	21.6/14.4		
ZnO/CuO				3.9	8.1/5.4		
CuO/ZnO				21.1	7.2/1.8		

of thin NFs.

Furthermore, higher responses were obtained by several authors [70, 71] when doping ZnO films. The dopants introduce important changes into the films, such as the microstructure, morphology, electrical characteristics, electronic structure, and specific surface area, hence improving their gas sensing performance. The Ca-doped ZnO thin films developed by Ghosh et al. [70] achieved a much higher sensitivity of 53 % at 350 $^{\circ}C$ and 50000 ppm of CO_2 but with high response/recovery times of 135/180 s. In addition, Marisol Gonz'alez-Garnica et al. [72] fabricated a hybrid Au-ZnO one-dimensional nanostructure grown onto Al-doped ZnO seed layer pre-deposited onto Si substrates, reaching a

very high sensitivity of 80 % at 250 $^{\circ}C$ and 200 ppm CO_2 with response/recovery times of 70/60 s, respectively.

For CuO-based sensors for CO_2 detection, a disparity in the reported results was observed in the literature (Table 4) [73], in terms of sensitivity and response time, depending on several factors such as the thickness of the CuO layer, detection temperature, humidity, etc. Bhowmick et al. [74] deposited a 250 nm thin film of CuO by sol-gel onto glass substrate and observed no reaction to CO_2 for temperatures below 250 $^{\circ}C$. A noticeable enhancement was observed when increasing the temperature from 250 to 300 $^{\circ}C$ and under a very high CO_2 concentration of 8354 ppm, the response doubled from 10 % to 21 % and

much lower response/recovery time of 5/5 s at 300 °C. However, this response time is equivalent to that obtained in this work, but at a much lower operating temperature of 25 °C. Atta Maki et al. [75] showed that a thickness of CuO layer larger 200 nm is needed to reaching a sensor response of 14 % at 500 ppm CO₂ and room temperature, but no reaction was observed for a smaller thickness in the range of 100–150 nm [75]. In addition, Chetoui et al. [76] prepared a thick 2 µm CuO film using spray pyrolysis, and obtained a very low sensor response of 3.5 % at 100 ppm CO₂ and room temperature. However, Kasian, P. and S. Pukird grown CuO nanowires (diameter 10–50 nm, length of 10 µm) by thermal evaporation and achieved an excellent sensor response of 101 % under a very low CO₂ concentration of 1.05 ppm and at a much higher temperature 400 °C [77].

In Table 4, the sensing response of bi-layered CuO/ZnO films was reported for comparison. It is noted that the combination of ZnO and CuO was investigated by several authors in different configurations as composite thin films, bi-/multi-layered thin films, as well as mechanical contact between CuO and ZnO. In this work, the maximum sensitivity obtained for the bi-layered CuO/ZnO and ZnO/CuO films at 25 °C are 6.5 and 21 %, respectively, which highlights clearly the critical effect of the top/under layer on sensor response.

Moreover, the sensing characteristics reported by Bhowmick et al. [7] and Musa et al. [2] demonstrated a poor performance compared to the values obtained in this study. Indeed, the CuO/ZnO film with a porous CuO top layer deposited onto glass substrate, as reported by T. Bhowmick et al. [7], demonstrated a response of 47 % at 375 °C, but for a very high CO₂ concentration of 2500 ppm. Musa et al. [2] reported that the deposited ZnO/CuO films onto glass substrates by dip-coating exhibited a high sensing response of ~48 % at room temperature when exposed to an extremely high CO₂ concentration of 10,000 ppm, but also both response/recovery times were very high (~3/~11 min). Similarly, Nakamura et al. [78] fabricated a CuO/ZnO hetero-contact sensor by a mechanical contact between CuO and ZnO pellets using a mechanical press and examined its sensing characteristics towards CO, CO₂, H₂, and C₃H₈ gases. The CuO/ZnO sensor showed a sensitivity of 30 % for a CO₂ concentration of 1000 ppm, a bias potential of 0.5 V, and 300 °C. This value is close to the value obtained in the present work for ZnO/CuO. However, the authors found that mechanical contacts in the bulk of the sensors limit the interaction area between CuO and ZnO layers, thereby affecting the sensor response. The high response obtained by Bhowmick et al. [7] can be explained by the generation of an n-p type CuO/ZnO heterojunction. In this configuration, the holes in p-CuO move toward the n-ZnO whereas the electrons move in the opposite direction until their Fermi level reaches equilibrium. Therefore, the depletion layer formed at the interface decreases the initial conductivity and enhances its response to the tested gas.

3.6. Sensing mechanism

For n-type or p-type metal oxides, the sensing mechanism relies on the reversible adsorption/desorption of gas molecules occurring on the sensor surface, accompanied by a change in the surface electrical resistance (current) [79]. For example, an n-type ZnO sensor exposed to air, oxygen is exclusively adsorbed as oxygen ions (O⁻, O₂⁻ or O₂²⁻ depending on the operating temperature) upon capturing electrons from the metal oxide surface [80,81]. However, for temperatures below 100 °C, as is the case in this work, oxygen molecules acquire only a single electron, as follows [82]:



These ionized oxygen species will penetrate the host lattice of metal oxide and subsequently produce oxygen vacancies behaving as electron donors, and the excess electrons are transferred to the doped ZnO film. This will improve the mobility of the charge carriers (electrons) and reduce the overall electrical resistance. Furthermore, upon CO₂ gas is in contact with the sensor, it chemisorbs onto the ZnO surface, captures

some electrons from the ZnO host lattice, and as a result a carbonate compounds like (CO₃)₂ is formed. Such type of interaction induces an important reduction in the number of available charge carriers, consequently decreasing the electrical conductivity (increase in resistance). Thus, this variation in the electrical resistance (current) serves as a gas detection signal and reflects the presence of CO₂ in the environment. However, when switching off CO₂, the previously formed carbonate complexes transform into CO₂, then the trapped electrons return to the sensor film's conduction band to occupy their original state.

For a p-type material, in this case p-CuO, the reverse phenomenon takes place. It is observed that the adsorption of charged oxygen species onto the sensor surface following the transfer of electrons from the p-type CuO. Consequently, the hole (as charge carriers) accumulation layer formed close to the surface, will cover the entire surface and lower the overall resistance [82,83]. When the p-type CuO is exposed to CO₂ gas, reactions occurring at the surface will cause a reduction in the charge carriers, increasing in the electrical resistance of the CuO thin film. For instance, the CuO sensor response to CO₂ of 21 % is found slightly higher than that obtained by Sameer Atta Maki et al., where the authors reported a value of 14 % at room temperature for a thickness of 200 nm [75]. In addition, the 250 nm CuO thin film fabricated by Bhowmick et al. [84], using the sol-gel method, the sensor did not react to CO₂ for temperatures below 250 °C. A response time in the range 10–21 % was achieved for temperatures 250–300 °C. For bi-layered ZnO/CuO and CuO/ZnO sensors, the reduction in the response time up to 8 s and 7 s respectively, compared to single-layered ZnO or CuO sensors, suggests a detection mechanism involving the contribution of the two layers (top and lower layers). In addition, by activating the reactions of oxygen chemisorption and surface catalysis, the sensor response is effectively enhanced at high temperatures above 200 °C.

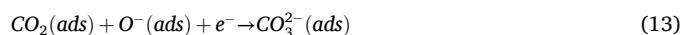
3.6.1. Gas sensing mechanism for CO₂ in Bi-layered structures

The sensing mechanism of the bi-layered metal oxide structures (ZnO/CuO and CuO/ZnO) towards carbon dioxide (CO₂) can be attributed to the surface adsorption and weak redox interactions between the target gas and pre-adsorbed oxygen species. In both cases, the bilayer configuration leads to the formation of two heterojunctions (P–N and N–P), which significantly influence charge carrier distribution, and the overall resistance change upon gas exposure (see Fig. 9).

In air, oxygen molecules are adsorbed on the surface of the metal oxides and extract electrons from the conduction band (in ZnO) or interact with holes (in CuO), forming ionized oxygen species as follows:



When exposed to CO₂, although the gas is relatively inert compared to reducing gases like CO or H₂, it can still interact with these adsorbed oxygen species. The following surface reaction is proposed:



This reaction consumes electrons, leading to a modification in the depletion or accumulation layers at the surface:

- In the ZnO/CuO structure (n-type on top): electrons are withdrawn from ZnO, increasing the depletion layer width and resulting in higher resistance.
- In the CuO/ZnO structure (p-type on top): the interaction may enhance hole concentration or alter the potential barrier, causing a decrease in resistance.

These opposite behaviors explain the difference in sensitivity between both two bilayer configurations. The role of the heterojunctions is

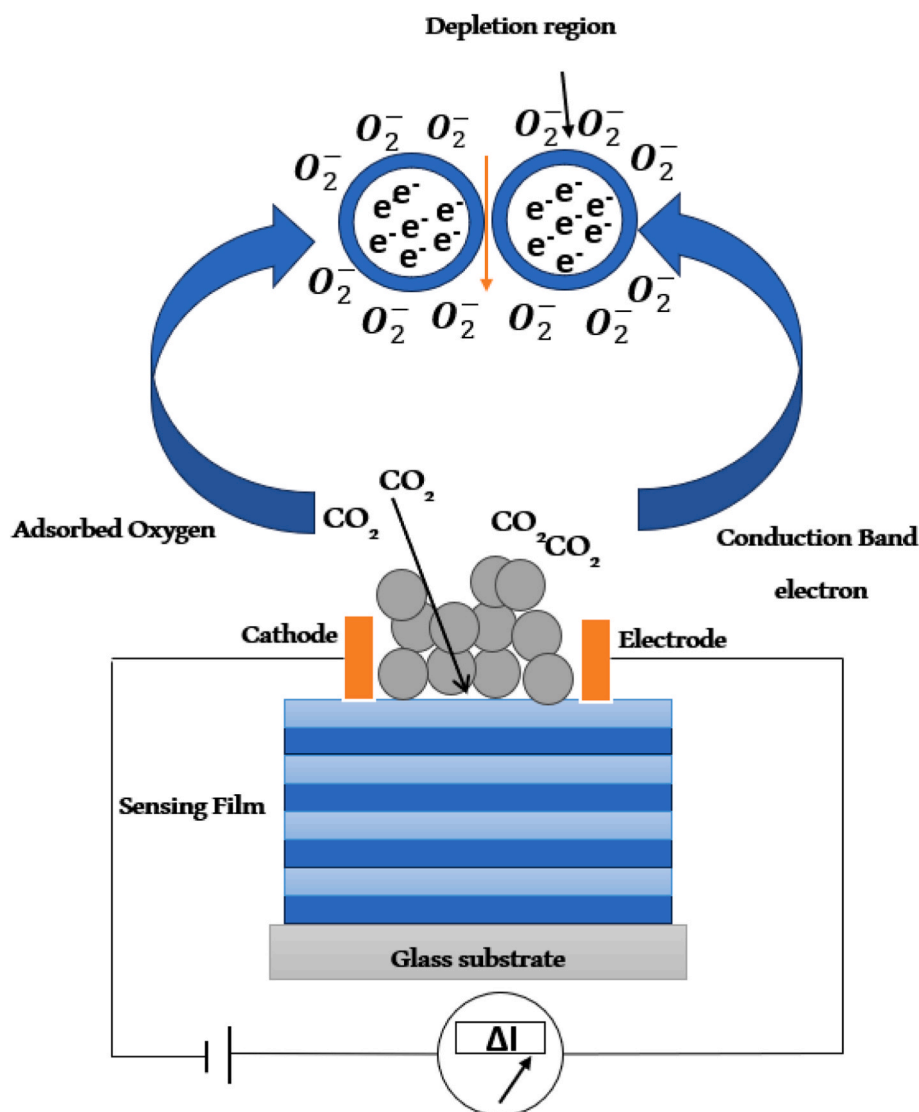


Fig. 9. The proposed sensing mechanism.

crucial, as they affect the direction of electron flow, band alignment, and modulation of the sensing signal.

4. Conclusion

Single-layered (ZnO, CuO) and bi-layered (ZnO/CuO and CuO/ZnO) thin film sensors were fabricated by cost-effective sol-gel dip-coating for room temperature CO₂ sensing. X-ray diffraction analysis confirmed the formation of polycrystalline CuO and ZnO phases. Further analyses by Raman and FT-IR spectroscopies revealed characteristic bands belonging to both phases in addition to functional groups. The ZnO film exhibited the smallest (~ 1 nm) roughness while CuO had the highest (~ 108 nm). The gas sensing tests towards CO₂ revealed that ZnO thin film demonstrated superior performance compared to CuO, ZnO/CuO, and CuO/ZnO. Indeed, the highest sensitivity of 44.8 % at 31 ppm CO₂ was achieved for ZnO, followed by 21.1 % for CuO/ZnO film at the same concentration. As for CuO and ZnO/CuO sensors, the sensitivity was found to be 19.3 % at 46.5 ppm CO₂, but a much lower value of 6.00 % for ZnO/CuO at the same CO₂ concentration. Nevertheless, both response/recovery times were found to be fast for all sensors, i.e., 6.0–46.2 s and 0.86–33.55 s, respectively.

Interestingly, the CuO/ZnO (ZnO top layer) bilayer displayed a sensitivity five times higher than the ZnO/CuO (CuO top layer)

structure, suggesting that the response of the p-n heterojunction is greater than that of the n-p heterojunction. Despite this, bilayer architectures remain promising for gas sensing applications. They offer insights into interface effects and the role of layer ordering. Continued optimization of material combinations and deposition strategies is essential for leveraging their full potential. Further studies are needed to elucidate the underlying sensing mechanisms and improve the performance of multilayer thin film sensors.

CRediT authorship contribution statement

Selwa Kebaili: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Sabrina Iaiche:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Faycal Bensouici:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Abdelkader Djelloul:** Validation, Supervision. **Stefano Bellucci:** Writing – review & editing, Validation, Supervision. **Fatima Boudeffar:** Methodology, Investigation. **Hocine Cheraga:** Methodology, Investigation. **Nour Eddine Gabouze:** Writing – review & editing, Validation. **Mohamed Bououdina:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

References

- Monthly atmospheric CO₂ concentration 2024, retrieved May 29, 2024 from, www.statista.com/téléchargementn.d, 2024.
- A.M.M. Musa, M. Rasadujaman, M.A. Gafur, A.T.M.K. Jamil, Synthesis and characterization of dip-coated ZnO–CuO composite thin film for room-temperature CO₂ gas sensing, *Thin Solid Films* 773 (2023) 139838, <https://doi.org/10.1016/j.tsf.2023.139838>.
- K. Fan, H. Qin, L. Wang, L. Ju, J. Hu, CO₂ gas sensors based on La_{1-x}Sr_xFeO₃ nanocrystalline powders, *Sens. Actuators, B* 177 (2013) 265–269, <https://doi.org/10.1016/j.snb.2012.11.004>.
- G.F. Fine, L.M. Cavanagh, A. Afonja, R. Binions, Metal oxide semi-conductor gas sensors in environmental monitoring, 5469–5502, <https://doi.org/10.3390/s100605469>, 2010.
- M. Casas-Cabanas, A.V. Chadwick, M.R. Palacín, C.R. Michel, Carbon dioxide sensing properties of bismuth cobaltite, *Sens. Actuators, B* 157 (2011) 380–387, <https://doi.org/10.1016/j.snb.2011.04.060>.
- V. National, Global Warming, Climate Change, Fossil Fuels and Anthropogenic Activities Have Warmed the, 2022.
- T. Bhowmick, A. Ghosh, S. Nag, S.B. Majumder, Sensitive and selective CO₂ gas sensor based on CuO/ZnO bilayer thin-film architecture, *J. Alloys Compd.* 903 (2022) 163871, <https://doi.org/10.1016/j.jallcom.2022.163871>.
- K. Zhao, G. Gu, Y. Zhang, B. Zhang, F. Yang, L. Zhao, et al., The self-powered CO₂ gas sensor based on gas discharge induced by triboelectric nanogenerator, *Nano Energy* 53 (2018) 898–905, <https://doi.org/10.1016/j.nanoen.2018.09.057>.
- S. Bouachma, K. Ayouz-Chebout, M. Kechouane, A. Manseri, C. Yaddadene, H. Menari, et al., Synthesis of PSI-n/CuO-p/Cu₂O-n heterostructure for CO₂ gas sensing at room temperature, *Appl. Phys. A Mater. Sci. Process.* 128 (2022), <https://doi.org/10.1007/s00339-021-05167-4>.
- K. M, N.H.N. Bourenane, N. Gabouze, Macroporous silicon (MPS) with embedded NiO thin film for CO₂ gas, *Arabian J. Sci. Eng.* (2018), <https://doi.org/10.1007/s13369-018-3264-5>.
- M. Habib, S.S. Hussain, S. Riaz, S. Naseem, Preparation and Characterization of ZnO Nanowires and their Applications in CO₂ Gas Sensors, 2, Elsevier Ltd., 2015, <https://doi.org/10.1016/j.matpr.2015.11.116>.
- Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reschikov, S. Doğan, et al., A comprehensive review of ZnO materials and devices, *J. Appl. Phys.* 98 (2005) 1–103, <https://doi.org/10.1063/1.1992666>.
- P. Taylor, G. Eranna, B.C. Joshi, D.P. Runthala, R.P. Gupta, G. Eranna, et al., Critical reviews in solid state and materials sciences oxide materials for development of integrated gas sensors — a comprehensive review oxide materials for development of integrated gas sensors — a comprehensive review, 37–41, <https://doi.org/10.1080/10408430490888977>, 2010.
- S. Yang, G. Lei, H. Xu, Z. Lan, Z. Wang, Metal Oxide Based Heterojunctions for Gas Sensors : a Review, 1–26, 2021.
- C.S. Dandaneau, Y.H. Jeon, C.T. Shelton, T.K. Plant, D.P. Cann, B.J. Gibbons, Thin film chemical sensors based on p-CuO/n-ZnO heterocontacts, *Thin Solid Films* 517 (2009) 4448–4454, <https://doi.org/10.1016/j.tsf.2009.01.054>.
- N. Batra, M. Tomar, V. Gupta, ZnO–CuO composite matrix based reagentless biosensor for detection of total cholesterol, *Biosens. Bioelectron.* 67 (2015) 263–271, <https://doi.org/10.1016/j.bios.2014.08.029>.
- E. Velayi, R. Norouzebeigi, Fabrication of fluorine-free ZnO/CuO nanocomposite superantwetting surfaces with reversible wettability tuning, *Surf. Coating Technol.* 367 (2019) 252–261, <https://doi.org/10.1016/j.surfcoat.2019.04.007>.
- A. Ch, K.V. Rao, C.H.S. Chakra, Synthesis and characterization of ZnO/CuO nanocomposite for humidity sensor application, *Adv. Mater. Proc.* 1 (2021) 60–64, <https://doi.org/10.5185/amp.2016/111>.
- S. Obregón, V. Rodríguez-González, Photocatalytic TiO₂ thin films and coatings prepared by sol–gel processing: a brief review, *J. Sol. Gel Sci. Technol.* 102 (2022) 125–141, <https://doi.org/10.1007/s10971-021-05628-5>.
- M. Faustini, B. Louis, P.A. Albouy, M. Kuemmel, D. Grosso, Preparation of sol–Gel films by dip-coating in extreme conditions, *J. Phys. Chem. C* 114 (2010) 7637–7645, <https://doi.org/10.1021/jp9114755>.
- F. Bensouici, T. Mahdia, Properties of ZnO thin films effect of Er₃ + doping on structural, morphological and photocatalytic properties of ZnO thin films manuscript version : accepted manuscript, <https://doi.org/10.1088/2053-1591/aac4e8>, 2018.
- R. Chouk, D. Haouanoh, C. Aguir, M. Bergaoui, M. Toubane, F. Bensouici, et al., Dye sensitized TiO₂ and ZnO charge transport layers for efficient planar perovskite solar cells: experimental and DFT insights, *J. Electron. Mater.* 49 (2020) 1396–1403, <https://doi.org/10.1007/s11664-019-07839-7>.
- MdJ. Uddin, MstS. Yeasmin, A.A. Muzahid, MdM. Rahman, G.M.M. Rana, T. A. Chowdhury, et al., Morphostructural studies of pure and mixed metal oxide nanoparticles of Cu with Ni and Zn, *Heliyon* 10 (2024) e30544, <https://doi.org/10.1016/j.heliyon.2024.e30544>.
- D.-K. Lee, K. Fykouras, T. Kodalle, R.F. Moral, C.P. Schwartz, N. Tamura, et al., Strain engineering: reduction of microstrain at the Perovskite surface via alkali metal chloride treatment enhances stability, *ACS Energy Lett.* 10 (2025) 1039–1049, <https://doi.org/10.1021/acseenergylett.4c03334>.
- P. Samarasekara, P.G.D.C.K. Karunaratna, B.M.C.M. Bandaranayake, J.S. T. Wickramasinghe, C.A.N. Fernando, Spin coated multilayered CuO/ZnO films with high output power under irradiation, *Mater. Res. Express* 6 (2018) 036415, <https://doi.org/10.1088/2053-1591/aaf7a5>.
- M. Gomathi, Study of dislocation density (defects such as Ag vacancies and interstitials) of silver nanoparticles. Green-Synthesized Using Barleria cristata Leaf Extract and the Impact of Defects on the Antibacterial Activity, 2018.
- O. Lupan, L. Chow, L.K. Ono, B.R. Cuenya, G. Chai, H. Khallaf, et al., Synthesis and characterization of Ag- or Sb-Doped ZnO nanorods by a facile hydrothermal route, *J. Phys. Chem. C* 114 (2010) 12401–12408, <https://doi.org/10.1021/jp910263n>.
- A. Dakhlaoui, M. Jendoubi, L.S. Smiri, A. Kanaev, N. Jouini, Synthesis, characterization and optical properties of ZnO nanoparticles with controlled size and morphology, *J. Cryst. Growth* 311 (2009) 3989–3996, <https://doi.org/10.1016/j.jcrysgro.2009.06.028>.
- S. Kunj, K. Sreenivas, Residual stress and defect content in magnetron sputtered ZnO films grown on unheated glass substrates, *Curr. Appl. Phys.* 16 (2016) 748–756, <https://doi.org/10.1016/j.cap.2016.04.008>.
- H. Zhou, L. Chen, V. Malik, C. Knies, D.M. Hofmann, K.P. Bhatti, et al., Raman studies of ZnO: co thin films, *Phys. Status Solidi (A) Appl. Mater. Sci.* 204 (2007) 112–117, <https://doi.org/10.1002/pssa.200673019>.
- S. Dolai, R. Dey, S. Das, S. Hussain, R. Bhar, A.K. Pal, Cupric oxide (CuO) thin films prepared by reactive d. c. Magnetron sputtering technique for photovoltaic application, *J. Alloys Compd.* 724 (2017) 456–464, <https://doi.org/10.1016/j.jallcom.2017.07.061>.
- H. Zhou, L. Chen, V. Malik, C. Knies, D.M. Hofmann, K.P. Bhatti, et al., Raman studies of znO:co thin films, *Phys. Status Solidi* 204 (2007) 112–117, <https://doi.org/10.1002/pssa.200673019>.
- P.S. Murthy, V.P. Venugopalan, D.A. Das, S. Dhara, R. Pandiyan, A.K. Tyagi, Antibiofilm Activity of Nano Sized CuO. International Conference on Nanoscience, Engineering and Technology (ICONSET 2011), IEEE, Chennai, 2011, pp. 580–583, <https://doi.org/10.1109/iconset.2011.6168037>.
- P. Sriyutha Murthy, V.P. Venugopalan, D.D. Arunya, S. Dhara, R. Pandiyan, A. K. Tyagi, Antibiofilm Activity of Nano Sized CuO. International Conference on Nanoscience, Engineering and Technology (ICONSET 2011), IEEE, Chennai, India, 2011, pp. 580–583, <https://doi.org/10.1109/ICONSET.2011.6168037>.
- A.G. Milekhin, N.A. Yeryukov, L.L. Sveshnikova, T.A. Duda, E.I. Zenkevich, S. Kosolobov, et al., Erratum to: "surface enhanced Raman scattering of light by ZnO nanostructures.", *J. Exp. Theor. Phys.* 114 (2012) <https://doi.org/10.1134/S1063776112010190>, 182–182.
- I. Musa, N. Qamhi, S.T. Mahmoud, Synthesis and length dependent photoluminescence property of zinc oxide nanorods, *Results Phys.* 7 (2017) 3552–3556, <https://doi.org/10.1016/j.rinp.2017.09.035>.
- F.J. Manjón, B. Marí, J. Serrano, A.H. Romero, Silent Raman modes in zinc oxide and related nitrides, *J. Appl. Phys.* 97 (2005) 053516, <https://doi.org/10.1063/1.1856222>.
- A. Calzolari, M.B. Nardelli, Dielectric properties and Raman spectra of ZnO from a first principles finite-differences/finite-fields approach, *Sci. Rep.* 3 (2013) 2999, <https://doi.org/10.1038/srep02999>.
- K.J. Chen, T.H. Fang, F.Y. Hung, L.W. Ji, S.J. Chang, S.J. Young, et al., The crystallization and physical properties of Al-doped ZnO nanoparticles, *Appl. Surf. Sci.* 254 (2008) 5791–5795, <https://doi.org/10.1016/j.apsusc.2008.03.080>.
- S. Iaiche, C. Boukaous, D. Alamarguy, A. Djelloul, D. Hamana, Effect of solution concentration on ZnO/ZnAl₂O₄ nanocomposite thin films formation deposited by ultrasonic spray pyrolysis on glass and Si(111) substrates, *JNANO* 63 (2020) 10–30, <https://doi.org/10.4028/www.scientific.net/JNANO.63.10>.
- S. Kunj, K. Sreenivas, Residual stress and defect content in magnetron sputtered ZnO films grown on unheated glass substrates, *Curr. Appl. Phys.* 16 (2016) 748–756, <https://doi.org/10.1016/j.cap.2016.04.008>.

- [42] P.A. Loiko, O.S. Dymshits, V.V. Vitkin, N.A. Skoptsov, A.A. Zhilin, D.V. Shemchuk, et al., Structure and nonlinear optical properties of novel transparent glass-ceramics based on Co^{2+} :ZnO nanocrystals, *Laser Phys. Lett.* 13 (2016) 055803, <https://doi.org/10.1088/1612-2011/13/5/055803>.
- [43] A. Fouchet, *Croissance Et Caractérisations De Films Minces De ZnO Et Zn Dopé Cobalt Préparés Par Ablation Laser Pulsé*, 2006.
- [44] J. Fang, Y. Xuan, Investigation of optical absorption and photothermal conversion characteristics of binary CuO/ZnO nanofluids, *RSC Adv.* 7 (2017) 56023–56033, <https://doi.org/10.1039/C7RA12022B>.
- [45] A. Dey, G. Chandrabose, P. Ghosh, L.A.O. Damptey, A.H. Clark, V. Selvaraj, et al., Atmospheric pressure plasma engineered superhydrophilic CuO surfaces with enhanced catalytic activities, *Appl. Surf. Sci.* 564 (2021) 150413, <https://doi.org/10.1016/j.apsusc.2021.150413>.
- [46] İ.Y. Erdoğan, The alloying effects on the structural and optical properties of nanocrystalline copper zinc oxide thin films fabricated by spin coating and annealing method, *J. Alloys Compd.* 502 (2010) 445–450, <https://doi.org/10.1016/j.jallcom.2010.04.193>.
- [47] T. Ivanova, A. Harizanova, T. Koutzarova, B. Vertruyen, R. Closset, Sol-gel synthesis of ZnO:Li thin films: impact of annealing on structural and optical properties, *Crystals* 14 (2023) 6, <https://doi.org/10.3390/cryst14010006>.
- [48] Iaiche S, Djelloul A. ZnO/ZnAl₂O₄ Nanocomposite Films Studied by X-Ray Diffraction, FTIR, and X-Ray Photoelectron Spectroscopy n.d.
- [49] J. Winiarski, W. Tytus, K. Winiarska, I. Szczygieł, B. Szczygieł, XPS and FT-IR characterization of selected synthetic corrosion products of zinc expected in neutral environment containing chloride ions, *J. Spectrosc.* 2018 (2018) 1–14, <https://doi.org/10.1155/2018/2079278>.
- [50] İ.Y. Erdoğan, Ö. Güllü, Optical and structural properties of CuO nanofilm: its diode application, *J. Alloys Compd.* 492 (2010) 378–383, <https://doi.org/10.1016/j.jallcom.2009.11.109>.
- [51] K. Ungeheuer, K.W. Marszalek, M. Mitura-Nowak, M. Perzanowski, P. Jelen, M. Marszalek, et al., Influence of Cr ion implantation on physical properties of CuO thin films, *IJMS* 23 (2022) 4541, <https://doi.org/10.3390/ijms23094541>.
- [52] L. Debbichi, De Lucas MC. Marco, J.F. Pierson, P. Krüger, Vibrational properties of CuO and Cu₄ O₃ from first-principles calculations, and raman and infrared spectroscopy, *J. Phys. Chem. C* 116 (2012) 10232–10237, <https://doi.org/10.1021/jp303096m>.
- [53] S. Saleem, A.H. Jabbar, M.H. Jameel, A. Rehman, Z.H. Kareem, A.H. Abbas, et al., Enhancement in structural, morphological, and optical properties of copper oxide for optoelectronic device applications, *Nanotechnol. Rev.* 11 (2022) 2827–2838, <https://doi.org/10.1515/ntrev-2022-0473>.
- [54] Balik M. Optical, Structural and Phase Transition Properties of Cu₂O, CuO and Cu₂O/CuO: Their Photoelectrochemical Sensor Applications n.d.
- [55] Alhumaimess MS, Essawy AA, Kamel MM, Alsouhaimi IH, Hassan HMA. Biogenic-Mediated Synthesis of Mesoporous Cu₂O/CuO Nano-Architectures of Superior Catalytic Reductive Towards Nitroaromatics n.d.
- [56] S.N. Narang, V.B. Kartha, N.D. Patel, Fourier transform infrared spectra and normal vibrations of CuO, *Phys. C Supercond.* 204 (1992) 8–14, [https://doi.org/10.1016/0921-4534\(92\)90566-U](https://doi.org/10.1016/0921-4534(92)90566-U).
- [57] Pillai S, Seery M, Georgekutty R. A Highly Efficient Ag-ZnO Photocatalyst: Synthesis, Properties, and Mechanism n.d.
- [58] F. Dabir, H. Esfahani, F. Bakhtiarionbadi, Z. Khodadadi, Study on microstructural and electro-optical properties of sol-gel derived pure and Al/Cu-doped ZnO thin films, *J. Sol. Gel Sci. Technol.* 96 (2020) 529–538, <https://doi.org/10.1007/s10971-020-05269-0>.
- [59] E. Bolli, A. Fornari, A. Bellucci, M. Mastellone, V. Valentini, A. Mezzi, et al., Room-temperature O₃ detection: zero-bias sensors based on ZnO thin films, *Crystals* 14 (2024) 90, <https://doi.org/10.3390/cryst14010090>.
- [60] D. Castillo-Vilcatoma, S. Loarte, A. Fernandez-Chillce, E. Pastrana, R. Pastrana, Designing and fabrication of a low-cost dip-coater for rapid production of uniform thin films, *Quim. Nova* (2021), <https://doi.org/10.21577/0100-4042.20170805>.
- [61] Spray Deposited Pure And CuO Doped ZnO Thin Films. n.d.
- [62] F. Bensouici, M. Bououdina, A.A. Dakhel, T. Souier, R. Tala-Ighil, M. Toubane, et al., Al doping effect on the morphological, structural and photocatalytic properties of TiO₂ thin layers, *Thin Solid Films* 616 (2016) 655–661, <https://doi.org/10.1016/j.tsf.2016.09.046>.
- [63] E. Chalangar, O. Nur, M. Willander, A. Gustafsson, H. Pettersson, Synthesis of vertically aligned ZnO nanorods using sol-gel seeding and colloidal lithography patterning, *Nanoscale Res. Lett.* 16 (2021) 46, <https://doi.org/10.1186/s11671-021-03500-7>.
- [64] N.M. Vuong, N.D. Chinh, B.T. Huy, Y.-I. Lee, CuO-Decorated ZnO hierarchical nanostructures as efficient and established sensing materials for H₂S gas sensors, *Sci. Rep.* 6 (2016) 26736, <https://doi.org/10.1038/srep26736>.
- [65] F. Boudjouan, A. Chelouche, T. Touam, D. Djouadi, R. Mahiou, G. Chadeyron, et al., Doping effect investigation of Li-doped nanostructured ZnO thin films prepared by sol-gel process, *J. Mater. Sci. Mater. Electron.* 27 (2016) 8040–8046, <https://doi.org/10.1007/s10854-016-4800-2>.
- [66] C. Ashok, K.V. Rao, C.S. Chakra, *Facile Synthesis and Characterization of ZnO/CuO Nanocomposite for Humidity Sensor Application*, 2016.
- [67] N. Zouadi, S. Messaci, S. Sam, D. Bradai, N. Gabouze, CO₂ detection with CNx thin films deposited on porous silicon, *Mater. Sci. Semicond. Process.* 29 (2015) 367–371, <https://doi.org/10.1016/j.mssp.2014.07.023>.
- [68] P.K. Kannan, R. Saraswathi, J.B.B. Rayappan, CO₂ gas sensing properties of DC reactive magnetron sputtered ZnO thin film, *Ceram. Int.* 40 (2014) 13115–13122, <https://doi.org/10.1016/j.ceramint.2014.05.011>.
- [69] S. Kanaparthi, S.G. Singh, Chemiresistive sensor based on zinc oxide nanoflakes for CO₂ detection, *ACS Appl. Nano Mater.* 2 (2019) 700–706, <https://doi.org/10.1021/acsanm.8b01763>.
- [70] A. Ghosh, C. Zhang, H. Zhang, S. Shi, CO₂ sensing behavior of calcium-doped ZnO thin film: a study to address the cross-sensitivity of CO₂ in H₂ and CO environment, *Langmuir* 35 (2019) 10267–10275, <https://doi.org/10.1021/acs.langmuir.9b00724>.
- [71] B. Ghanbari Shohany, L. Motevalizadeh, M. Ebrahimizadeh Abrishami, Investigation of ZnO thin-film sensing properties for CO₂ detection: effect of Mn doping, *J. Theor. Appl. Phys.* 12 (2018) 219–225, <https://doi.org/10.1007/s40094-018-0302-3>.
- [72] M. González-Garnica, A. Galdámez-Martínez, F. Malagón, C.D. Ramos, G. Santana, R. Abolhassani, et al., One dimensional Au-ZnO hybrid nanostructures based CO₂ detection: growth mechanism and role of the seed layer on sensing performance, *Sensor. Actuator. B Chem.* 337 (2021) 129765, <https://doi.org/10.1016/j.snb.2021.129765>.
- [73] C. Maier, L. Egger, A. Köck, K. Reichmann, A review of gas sensors for CO₂ based on copper oxides and their derivatives, *Sensors* 24 (2024) 5469, <https://doi.org/10.3390/s24175469>.
- [74] T. Bhowmick, A. Ghosh, V. Ambardekar, et al., Potential of copper oxide thin film-based sensor probe for carbon dioxide gas monitoring, *J. Mater. Sci. Mater. Electron.* 33 (2022) 26286–26298, <https://doi.org/10.1007/s10854-022-09312-4>.
- [75] S.A. Maki, O.A. Mahmoud, *The Thickness Effect of CuO Thin Films on Electrical and Gas Sensing Properties*, 4, 2017.
- [76] C. Abdelmounaim, Z. Amara, A. Maha, D. Mustapha, Effects of molarity on structural, optical, morphological and CO₂ gas sensing properties of nanostructured copper oxide films deposited by spray pyrolysis, *Mater. Sci. Semicond. Process.* 43 (2016) 214–221, <https://doi.org/10.1016/j.mssp.2015.12.019>.
- [77] P. Kasian, S. Pukird, Gas sensing properties of CuO nanostructures synthesized by thermal evaporation of copper metal plate, *AMR (Adv. Magn. Reson.)* 93–94 (2010) 316–319, <https://doi.org/10.4028/www.scientific.net/AMR.93-94.316>.
- [78] Y. Nakamura, H. Zhuang, A. Kishimoto, O. Okada, H. Yanagida, Enhanced CO and CO₂ gas sensitivity of the CuO/ZnO heterocontact made by quenched CuO ceramics, *J. Electrochem. Soc.* 145 (1998) 632–638, <https://doi.org/10.1149/1.1383315>.
- [79] H. Ji, W. Zeng, Y. Li, Gas sensing mechanisms of metal oxide semiconductors: a focus review, *Nanoscale* 11 (2019) 22664–22684, <https://doi.org/10.1039/C9NR07699A>.
- [80] D. Acharyya, P. Bhattacharyya, Alcohol sensing performance of ZnO hexagonal nanotubes at low temperatures: a qualitative understanding, *Sensor. Actuator. B Chem.* 228 (2016) 373–386, <https://doi.org/10.1016/j.snb.2016.01.035>.
- [81] P. Bhattacharyya, D. Acharyya, K. Dutta, Resistive and capacitive measurement of nano-structured gas sensors, in: N. Dasgupta, S. Ranjan, E. Lichtfouse (Eds.), *Environmental Nanotechnology*, 21, Springer International Publishing, Cham, 2019, pp. 25–62, https://doi.org/10.1007/978-3-319-98708-8_2.
- [82] Amiri V, Roshan H, Mirzaei A, Neri G, Ayeshe AI. Nanostructured Metal Oxide-based Acetone Gas Sensors: a Review n.d.
- [83] H.-J. Kim, J.-H. Lee, Highly sensitive and selective gas sensors using p-type oxide semiconductors: overview, *Sensor. Actuator. B Chem.* 192 (2014) 607–627, <https://doi.org/10.1016/j.snb.2013.11.005>.
- [84] T. Bhowmick, A. Ghosh, V. Ambardekar, S. Nag, S.B. Majumder, Potential of copper oxide thin film-based sensor probe for carbon dioxide gas monitoring, *J. Mater. Sci. Mater. Electron.* 33 (2022) 26286–26298, <https://doi.org/10.1007/s10854-022-09312-4>.