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Investigation on thermal annealing effect on the physical properties of CuO-SnO₂:F sprayed thin films for NO₂ gas sensor and solar cell simulation

Ghofrane Charrada ^{a,b,*}, Mejda Ajili ^a, Neila Jebbari ^a, Moez Hajji ^a, Sandrine Bernardini ^b, Khalifa Aguir ^b, Najoua Turki Kamoun ^a

^a Université de Tunis El Manar, Faculté des Sciences de Tunis, Département de Physique, LR99ES13 Laboratoire de Physique de La Matière Condensée (LPMC), 2092, Tunis, Tunisia

^b Aix Marseille Univ, CNRS, IM2NP, Marseille, France

* Corresponding author at: 96 Rue bachir nabheni dar chaaben, 8011 Nabeul, Tunisia.
E-mail address: ghofrane.2019.charrada@gmail.com (G. Charrada).

ABSTRACT

Thin films, owing to their versatility, are extensively employed in various applications, including solar cells and gas detection. In this study, CuO-SnO₂:F thin films were fabricated using spray method. The influence of annealing temperature on their properties was examined. X-ray diffraction analysis of post-annealing at 300 °C revealed the emergence of the Cu₂O phase, which disappeared at higher annealing temperatures of 500 °C. Substantial improvements in structural, optical, and electrical characteristics were observed, with the optimized films exhibiting heightened responsiveness at low NO₂ gas concentration (4 ppm). The optimum operating temperature was determined at 150 °C, demonstrating small response and recovery times, and good reproducibility. Furthermore, Silvaco TCAD simulation was employed to model CIGS (Copper Indium Gallium Selenide) solar cells incorporating CuO-SnO₂:F thin films as a buffer layer, yielding an impressive efficiency of 15.31 %.

Keywords:

Thin films Annealing temperature Sensors Physical properties Solar energy materials

1. Introduction

The utilization of metal oxides in optoelectronic applications, such as gas sensors and photovoltaic systems, represents a significant advancement in modern technology [1]. The evolution of CIGS solar cells represents a significant milestone in photovoltaics field, offering high efficiency and stability compared to traditional silicon-based solar cells [2]. However, the use of cadmium sulfide (CdS) as a buffer layer in CIGS cells has raised concerns due to its toxicity and environmental impact [3]. This necessity for alternative buffer layers has spurred research into new materials and designs to enhance the sustainability of solar energy technologies. Mixed oxide thin films have emerged as promising candidates for replacing CdS due to their lower toxicity and potential for improved performance. In gas sensor applications, to save the environment and human health, it is important to develop a sensitive and accurate gas sensor for monitoring harmful gases such as NO₂. Metal oxide thin films such as SnO₂, CuO, In₂O₃, while effective in NO₂ gas sensing, often suffer from the high working temperature (>300 °C) which restrict their commercial applications because it requires more resources and expensive costs [4]. The development of coupled oxide systems, such as CuO-SnO₂:F,

addresses this challenge by offering high surface area, making the operating temperature down, enhancing the sensor's sensitivity to target gases and improving its overall performance. Additionally, by exploring the potential of these materials as buffer layers in CIGS solar cells, this study contributes to the development of efficient optoelectronic devices for a cleaner energy future.

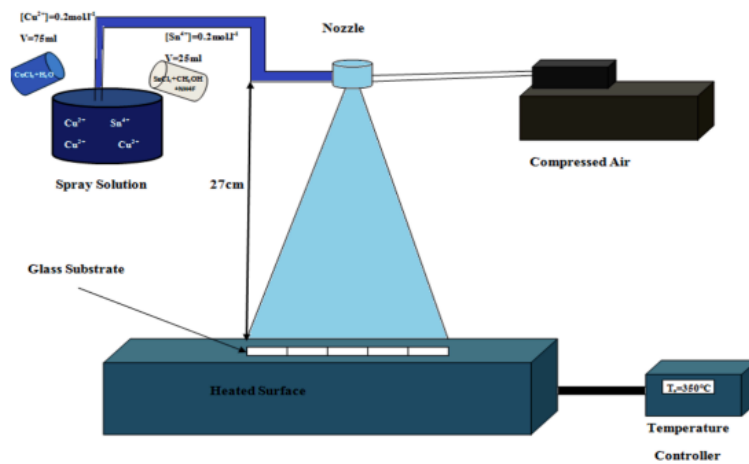
2. Experimental technique

CuO-SnO₂:F thin films were prepared using spray technique. CuO precursor solution (C = 0.2 mol.l⁻¹) was obtained by dissolving CuCl₂ in de-ionized water while SnO₂:F solution was prepared by dissolving SnCl₄ in methanol with the same concentration through the following chemical reactions:

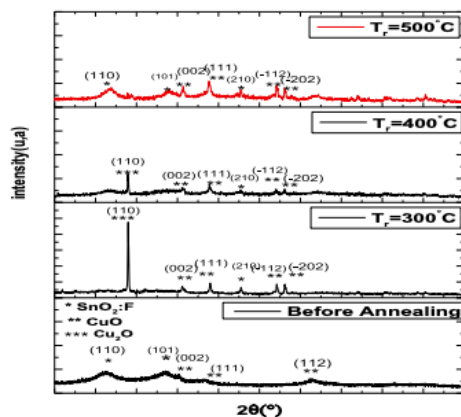


Next both solution (25 ml SnO₂:F solution + 75 ml of CuO solution) were mixed with a ratio equal to [Cu] [Sn] = 3 and sprayed at 350 °C (Fig. 1.a).

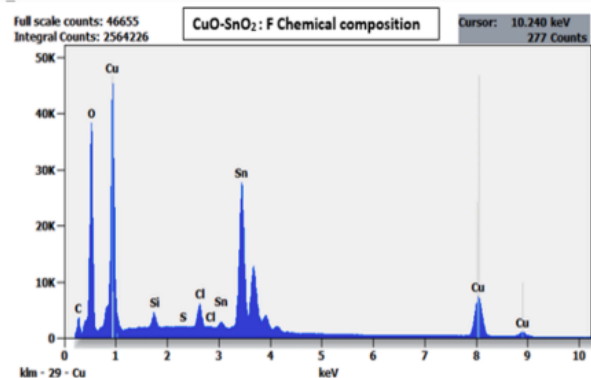
(a)



(b)



(c)



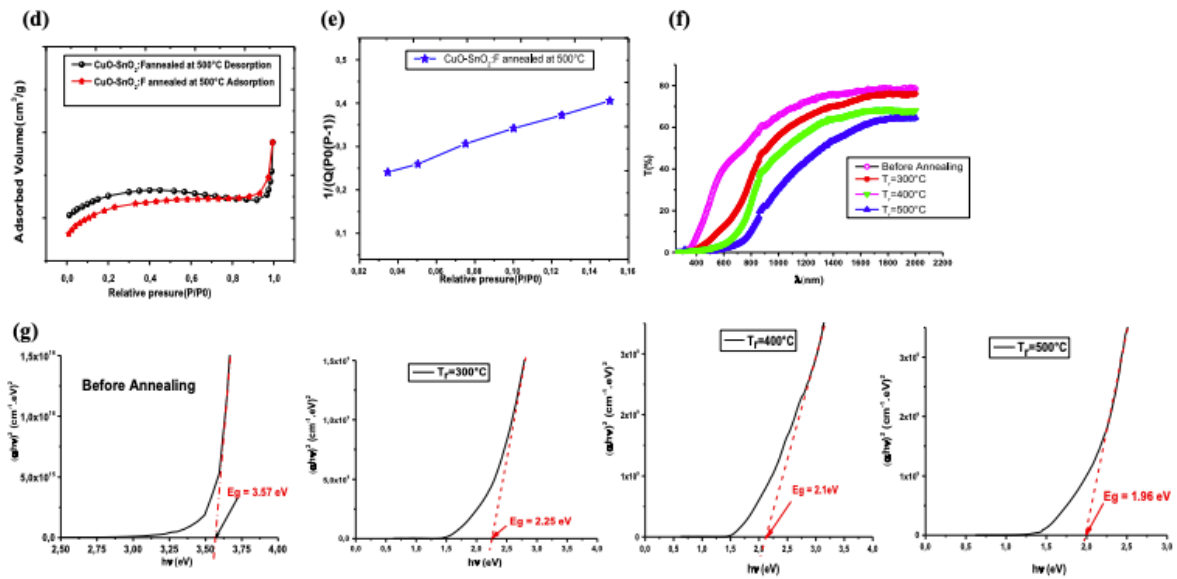


Fig. 1. (a) Chemical spray deposition (b) X-ray diffraction spectra (c) EDS Spectra (d) N₂-adsorption-desorption isotherm plots (e) BJH pore size distribution curve (f) Transmission (T) spectra, (g) Band gap energy of CuO-SnO₂: F thin films before and after annealing

Then, the films were annealed at various temperatures ranging from 300 to 500 °C during 2 h. Structural properties were determined by XRD patterns at room temperature using a diffractometer ($\lambda_{\text{Cu}} = 1.540 \text{ \AA}$). EDS analysis was studied using TS Quanta 250. Specific surface areas were calculated using a multipoint BET method, utilizing adsorption data employing a Micromeritics ASAP 2020 instrument. Optical properties were studied using a Perkin-Elmer Lambda 950 spectrophotometer. Furthermore, the ECOPIA Hall effect Measurement System was used to evaluate the electrical characteristics. Gas sensing measurements were performed using a Keithley (model 6514) electrometer to determine electrical resistance (1 V dc voltage was applied).

3. Results and discussion

3.1. Physical properties

We utilized X-ray diffraction technique to investigate the structural properties of CuO-SnO₂:F thin films and explored the impact of annealing temperatures on their crystalline structure. XRD spectra (Fig. 1.b) shows discernible peaks corresponding to SnO₂:F and CuO phases, signifying the successful synthesis of CuO-SnO₂:F thin layers, that can be confirmed by our previous research [5]. After annealing, the emergence of the Cu₂O phase is evident. However, this phase disappeared following annealing at 500 °C, accompanied by an improvement in crystallinity. In fact, the energy provided breaks down the Cu₂O phase into CuO, which is more stable at higher temperatures [6]. These findings underscore the significant influence of annealing temperature on the phase evolution and crystalline quality of the CuOSnO₂:F thin films, highlighting the nuanced interplay between thermal treatment and structural transformations. EDS spectra (Fig. 1.c) confirmed the presence of the expected elements Cu, Sn and O, along additional impurities associated with precursors (Cl) and glass substrate (S, Si and C). The BET adsorption isotherm, (Fig. 1.d) of samples annealed at 500 °C exhibited a type III hysteresis loop. Employing the standard multi-point BET method (Fig. 1.e), the surface

areas was calculated to be 14.32 m² /g. The transmission spectra, graphically depicted in Fig. 1.f, reveal noteworthy information about the material's optical properties. Notably, the intrinsic absorption shifts towards longer wavelengths by increasing heating temperature, indicating a potential for extended functionality in the near IR range. Furthermore, within the visible wavelength range, an observable trend is discerned as the transmittance values decrease with escalating annealing temperatures. Using transmission spectra, we proceeded to calculate the band gap energy using the Tauc formula (Fig. 1.g) [5]. A significant decrease in gap was observed from 3.57 eV to 1.96 eV after annealing at 500 °C, which can be attributed to multiple factors, including structural rearrangement, changes in crystal phase and interface effects between phases [6]. The electrical properties of CuO-SnO₂: F thin films before and after annealing at 500 °C were studied using the Hall Effect technique as shown in Table 1.

Table 1: Electrical parameters of CuO-SnO₂: F thin films before and after annealing at 500 °C.

Thin layer	Resistivity (Ω.cm)	Conductivity(Ω.cm) ⁻¹	Rh (cm ³ .C ⁻¹)	μ (cm ² .v ⁻¹ .s ⁻¹)	n _h (cm ⁻³)	Type of conductivity
CuO-SnO ₂ :F Before annealing	0.73	1.36	1.2*10 ⁵	1.36*10 ⁵	0.44*10 ¹⁴	p
CuO-SnO ₂ :F annealed at 500 °C	0.69	1.49	4.67*10 ⁵	6.95*10 ⁵	7.47*10 ¹⁴	p

The results revealed that the thin films exhibited low resistivity, high mobility and carrier hole density, suggesting efficient charge transport within the material. Moreover, an improvement of electrical parameters was obtained after annealing process.

3.2. Solar cell simulation and nitrogen dioxide gas sensor

t data obtained from modelling will be compared with experimental results. The structure and the mesh of our simulated solar cell are illustrated in Fig. 2.a and Fig. 2.b respectively.

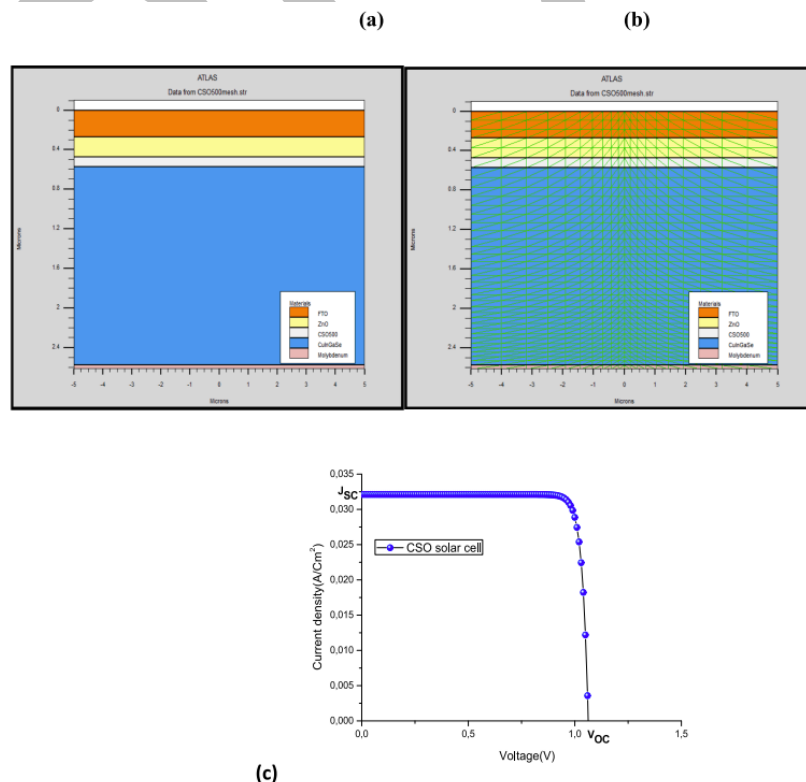


Fig. 2. Solar cell parameters based on CuO-SnO₂: F thin film annealed at 500 °C (a) structure (b) mesh (c) J-V curve.

Our solar cell structure comprises the following components: Molybdenum as an electrode layer, an n-type ZnO layer acting as window layer, p-type CIGS thin film serving as absorber layer, CuO-SnO₂:F annealed at 500 °C as buffer layer and a back contact layer of FTO deposited on the top of the structure. The (J-V) curve of the simulated solar cell is depicted in Fig. 2.c, revealing key performance parameters. Notably, a Voc (open-circuit voltage) of 0.72 V and a Jsc (short-circuit current density) of 0.033 A/ Cm² were observed, leading to an impressive efficiency of 15.31 %. These findings underscore the efficacy to use CuO-SnO₂: F as a buffer layer in order to enhance the overall performance of the solar cell. Despite previous studies indicating lower efficiency compared to CdS buffer layers [7]. Our choice to use CuO-SnO₂:F presents significant advantages in terms of economic viability and environmental impact. Unlike CdS, which is toxic and costly to produce, our thin film buffer layer offers a non-toxic and low-cost alternative. To protect public health, international standards dictate that NO₂ concentration in the surrounding atmosphere should not exceed 25 ppm, as exceeding this concentration represent a threat to human life [8]. Therefore, we have developed a sensitive and accurate gas sensor based on CuO-SnO₂:F thin films for nitrogen dioxide at extremely low concentration (4 ppm). Sensing tests were realized at varied operating temperatures from 50 °C to 250 °C to find out the optimum working temperature. Fig. 3.a shows the calculated gas response of the deposited films as a function of temperature. The gas response was increased with increasing operating temperature, which reached 1.2 at 150 °C, and decreased after. The good responsivity of CuO-SnO₂:F to NO₂ can be primarily attributed to its surface area, enabling the efficient adsorption of numerous NO₂ molecules. This relatively high surface area (14.32 m² /g) facilitates extensive interaction between gas molecules and active sites on the material's surface, enhancing sensitivity and responsiveness. Fig. 3.b. shows the resistance response curve of CuOSnO₂: F sensor exposed to 4 ppm NO₂ gas at low operating temperature of 150 °C. The CuO-SnO₂:F based sensor behave like p-type semi-conductors, their electrical resistance decreases upon to oxidant gas NO₂. CuO-SnO₂:F thin films demonstrate good stability, small response (48 s) and recovery times(138 s) to NO₂ gas sensor, as shown in Fig. 3.b, which makes them invaluable in environmental monitoring and Industrial safety applications.

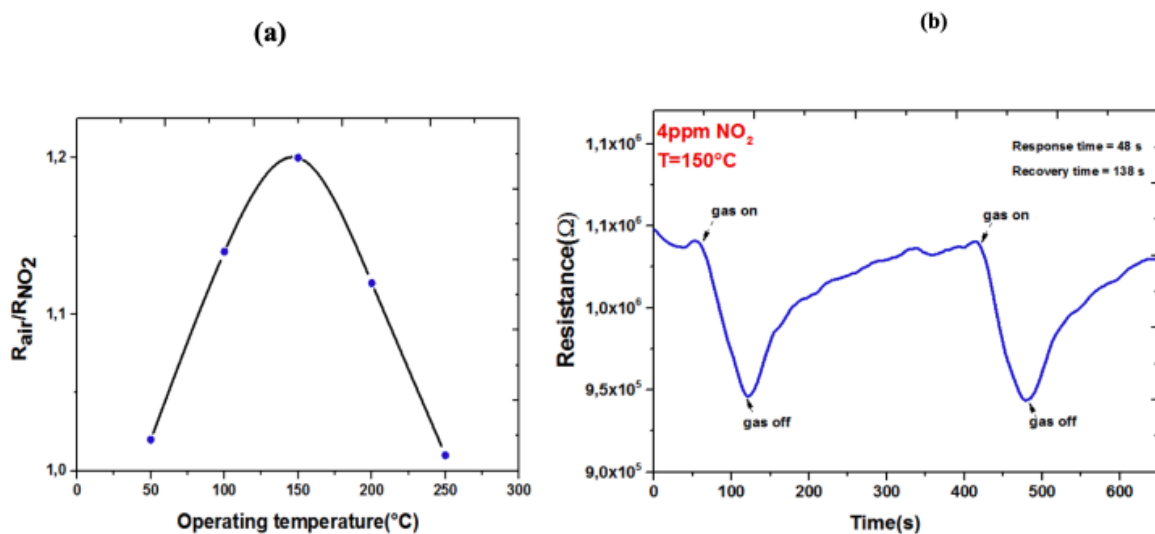


Fig. 3. (a) Variation in NO₂ response with operating temperatures (b) Response transient to 4 ppm NO₂ of CuO-SnO₂: F thin films at 150 °C.

The crystalline structure and interfacial characteristics of CuO-SnO₂:F ensure long-term performance without significant degradation, allowing it for reliable and accurate detection of NO₂ over extended periods.

4. Conclusion

In conclusion, the elaboration of CuO-SnO₂: F thin films succeeded by various annealing temperatures has proven to be a successful endeavor, yielding significant improvements in their physical properties. These advancements pave the way for their potential application as buffer layer in CIGS solar cells, demonstrating an impressive efficiency of 15.31 %. Moreover, these films exhibit a notable responsiveness to NO₂ gas at low concentrations and operating temperatures. As research progresses, further optimizations and refinements may unlock even greater potential for these materials in various practical applications.

Credit authorship contribution statement

Ghofrane Charrada: Writing – original draft. Mejda Ajili: Supervision. Neila Jebbari: Supervision. Moez Hajji: Data curation. Sandrine Bernardini: Supervision. Khalifa Aguir: Visualization, Supervision. Najoua Turki Kamoun: 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.

Data availability

No data was used for the research described in the article

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