

Thin Films for Advancements in Gas Sensing Technologies

Eleonora Bolli¹, Alice Fornari¹, Matteo Mastellone^{1,2}, Raffaella Salerno³, Veronica Valentini¹, Riccardo Polini³, Antonio Santagata², Maria L. Pace², Alessandro Bellucci¹ and Daniele M. Trucchi¹

¹ ISM-CNR, Institute of Structure of Matter, DiaTHEMA Lab, Monterotondo Scalo (RM), 00015 Italy

² ISM-CNR, Institute of Structure of Matter, FemtoLAB, Tito Scalo, Zona Industriale, 85050 Tito, Italy

³ Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma 'Tor Vergata', 00133 Rome, Italy

Abstract The transition from conventional bulk materials to materials with size- and shape-dependent surface properties such as nanostructured materials, nanoparticles, and thin films have opened the way to a new generation of gas sensors characterized by enhanced sensitivity, selectivity, and rapid response. Thin films, with their unique properties, offering functionalized surfaces through precise control of parameters such as thickness, grain size, and composition, by selecting the proper substrate material and deposition methods can address these requirements. In this scenario increased surface-to-volume ratio of nanostructured thin films make them ideal for detecting a wide range of gases. Moreover, the reduced size facilitates cost-effective production processes and seamless integration into devices, enabling constant remote monitoring and wireless data collection. This study explores the use of thin films in gas sensors employing metal oxide semiconductors (MOXs). MOX sensors, particularly those based on SnO₂, ZnO, and WO₃, stand out for their high surface sensitivity and stability. Their chemiresistor behaviour, where electronic properties change upon the adsorption of gas molecules, enables precise detection of harmful gases by measuring variations in electrical resistivity. The possibility of operating at room temperature, together with a high sensitivity due to enhanced nanostructuring, represents a viable solution to the increasing demand for monitoring air pollution.

Keywords: MOX sensors, thin films, gas sensors, heterostructures, nanostructured materials

1. Introduction

The evolution of gas sensors has been closely linked to human progress since the Industrial Revolution in the 18th century. However, only during the 1950s that solid-state gas sensors, primarily composed of semiconductors, had emerged. With the advent of the 21st century and the rise of nanotechnologies, there was a significant shift from bulk materials with good intrinsic properties to those where behaviours are strongly affected by the low surface dimensionality [1,2].

Today, the demand for monitoring air pollutants, such as CO₂, NO₂, and O₃, is critical for outdoor and indoor environmental protection, industrial safety, and healthcare. Thin films, which have demonstrated their applicability in various environmental and energy scientific fields such as thermoelectric [3-5] and thermionic applications [6-11], are nowadays proposed as excellent candidates for use as sensitive materials in gas sensors [12]. Thanks to their increased surface-to-volume ratio, thin films exhibit enhanced sensitivity, selectivity, and response readiness. They also enable low-cost production and easy integration into devices, making them well-suited for the latest innovations, such as Internet of Things (IoT) technology for continuous remote gas monitoring [13]. Metal oxide semiconductors (MOXs) like SnO₂, ZnO, and WO₃ detect gases through chemiresistor behaviour, changing electrical resistivity upon gas molecule adsorption [14]. Although they are effective for gas detection, high operating temperatures (300–500 °C) are usually needed for optimal sensitivity [1,14]. However, film performance can be significantly influenced by the deposition methods used [12,15]. By applying specific techniques and even post-deposition technological approaches for optimization, the working temperature allowing optimal operation can be reduced

down to room temperature. In such conditions the stability and longevity of the device, as well as the technical constraints for the design of the electronic board of sensors, can be achieved [16].

This paper focuses on the advancements in gas sensing technologies, particularly on the deposition methods and post-deposition treatments used to tailor the surface of MOX thin films for gas sensing at room temperature in indoor applications as smart buildings.

2. Materials and Methods

2.1 Thin film deposition

Several physical vapor deposition techniques have been investigated for the deposition of thin films. RF magnetron sputtering (RF-MS) is a widely used thin film deposition technique that uses radio frequency power to generate plasma, enabling the sputtering of a target material onto a substrate and producing high-quality, uniform coatings. As a result, RF-MS provides excellent thickness control [15]. Another physical deposition method is electron-beam evaporation (EBE), where an electron beam heats and locally evaporates a target material, which then condenses onto a substrate, so that high-purity films are formed. EBE produces polycrystalline films with high surface areas [12]. Finally, pulsed laser deposition (PLD) is a technique where a high-power laser pulse ablates material from a target, which then deposits onto a substrate, thus forming a thin film with high crystallinity if suitable process parameters are selected [15]. The right choice of deposition technique allows control over key film properties such as grain size, thickness, crystallinity, and porosity, which can significantly improve the performance of a gas sensor, as demonstrated in the cited reference works [12,15].

2.2 Defect Engineering and Composed materials to improve gas sensor's performance

Defect engineering is a strategic approach in materials science used to manipulate and control the properties of materials by intentionally introducing and managing defects. This technique is particularly effective for optimizing the properties of surfaces in gas sensor technologies thanks to the possibility to alter the band structure, carrier concentration, and mobility. Key techniques for defect engineering include thermal annealing [17] and various surface treatments such as innovative solution recently proposed where femtosecond (fs) laser treatments are employed. These treatments modify the surface morphology by producing well-organized and periodic geometrical features, as shown in tin oxide-based sensors for CO₂ detection at room temperature [18]. Another approach involves composite and multilayer materials. Recent studies have shown that p-n heterojunctions can enhance the charge transport, thereby resulting in a improvement of the gas sensitivity of MOX thin films. Advanced results of thin films forming p-n heterojunctions are reported in recent papers [18-20]. Additionally, in this work the strategy in using multilayer thin films made from different materials will be introduced.

2.3 Gas Sensing

The gas sensitivity tests of all the sensors cited in this work were conducted on devices comprising thin films or multilayer materials (the sensitive part of the sensor) deposited on an alumina printed-circuit board (PCB) produced by CERcuits BV (Geel, Belgium). The gas sensor tests were performed using a commercial glove box (Cole-Parmer Instrument Company, LLC, UK) with a volume of about 0.25 m³, suitable for maintaining confined gas concentrations.

Thanks to a customized flowmeter system (Ionvac Process srl, Pomezia, Italy), it was possible to regulate the flow of each gas in the chamber, which was then evacuated by a membrane pump (pressure of $\sim 10^{-1}$ mbar) to ensure stable conditions and fast removal of pollutants. The experimental setup was described in detail in a previous work [12].

Results and Discussion

Table 1 summarizes the recent results obtained by our group with MOX thin film sensors deposited on alumina substrate using different techniques and testing various types of potentially hazardous gases present in air. All these solutions have the advantage to operate at room temperature.

Table 1 Results

MOX thin film	Deposition Method	Target Gas	Response time	Recovery time	Range Tested	Threshold for health	Sensitivity (%)	Refs.
ZnO	MS	O ₃	< 4s	< 15 min	55-1150 ppb	50 ppb	30 % at 100 ppb	Not published
ZnO	EBE	O ₃	< 2s	< 15 s	55-1150 ppb	50 ppb	10 % at 55 ppb	[12]
WO ₃	PLD	NO ₂	< 20 s	< 80 s	5-20 ppm	10 ppm		[17]
SnO-SnO ₂ as deposited	EBE	CO ₂	< 2s	< 120 s	110-5000 ppm	1500 ppm	15 % at 1000 ppm	[18]
SnO-SnO ₂	EBE + fs-treated	CO ₂	< 2s	infinite	110-5000 ppm	1500 ppm	15 % at 5000 ppm	[18]
Multilayer	EBE	CO ₂	< commercial sensor	< commercial sensor	500-1200 ppm	1500 ppm	50 % At 800 ppm	This work

In the previous works, we found that all the deposition techniques provide nanostructured materials, with the achievement of promising results in terms of both response readiness and recovery rates. However, the sensitivity values are in line with other proposed structures present in literature, and, above all, no real tests out-of-the-lab were made to assess either reliability or durability.

For this work, a sensor composed of multilayer thin films of SnO - ZnO - SnO (300-100-300 nm of thickness) was deposited on alumina substrate using the EBE technique. The multilayer was characterized by Raman spectroscopy (see Figure 1), which confirmed the presence of both compounds, that means: 1) two bands, B1g = 112 cm⁻¹ and A1g = 210 cm⁻¹ which are related to SnO species; one band centered at around 560 cm⁻¹ due to the B1(high) vibration corresponding to the ZnO cubic structure (zincblende) induced by the growth carried out by EBE [12].

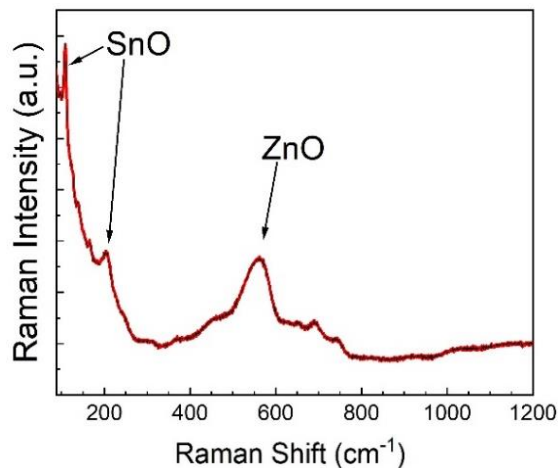


Figure 1. Raman spectrum of multilayer SnO-ZnO-SnO sample.

This multilayer was tested during a measurement campaign carried out in a primary school. The signal from this prototype was always compared with that provided by a commercial sensor (see Figure 2), showing response and recovery times that were equal or even faster than those of the commercial sensor based on a different technology (NDIR). Peaks in [CO₂] were observed during the daytime, when students and school personnel staff were present in the building. The tests demonstrated that the prototype remained stable throughout the entire week, stabilizing to the ground level CO₂ concentration of around 500 ppm when the building was closed during the night, with peaks reaching 1200 ppm during crowded periods such as school entrance and exit times. Our prototype seems to

have a lower sensitivity with respect to the commercial sensor (which is considered reliable with a resolution of 0.6 ppm and a lowest detection threshold of 1 ppm according to the datasheet [21]), estimating however a sensitivity of 50% at 800 ppm.

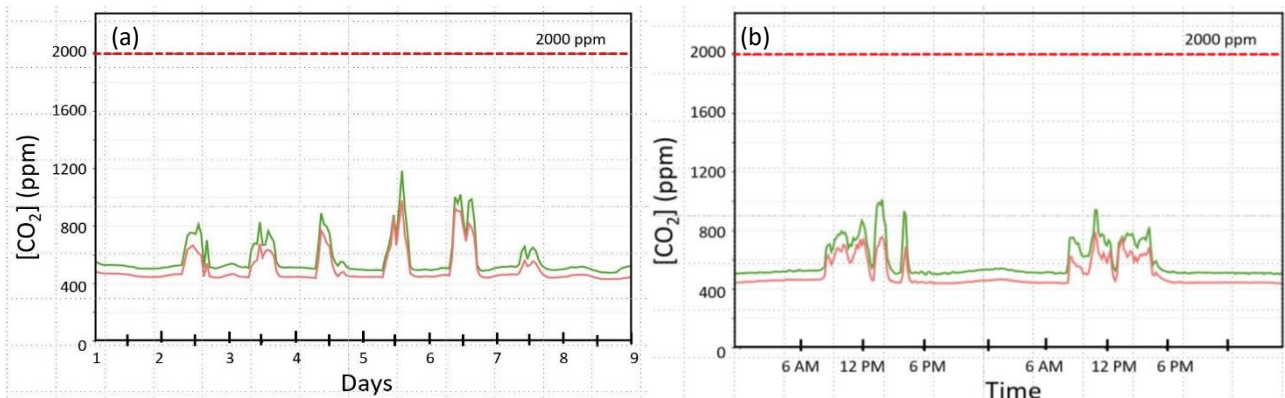


Figure 2. (a) CO₂ sensitivity measurement campaign conducted for 8 days in a primary school of the Montemurro city (Basilicata, South Italy). Multilayer sensor signal (red line) compared with the signal from a commercial sensor (NDIR technology, AQ Safe, green line); (b) Detailed gas concentration data for two specific days.

3 Conclusions

As it is shown by the results obtained from the recent developed MOX thin films, MS, EBE, and PLD can be considered to be promising techniques for obtaining nanostructured thin films with good gas sensing performance at room temperature. Multilayer sensors produced by EBE have finally been tested and continuously monitored using an IoT network in the framework of the IBIS ECO project, by showing a behaviour very similar to commercial sensors based on a different technology. These tests demonstrate the potential of the produced sensors, which can operate at room temperature with lower energy consumption, and low costs at the mass-market scale. Finally, advanced nanostructuring techniques like fs-laser treatments can further enhance the device performance so that, in the near future, the role innovative gas sensor devices can be applied in the real life.

Acknowledgement

This research was conducted as part of the IBIS ECO “IoT-based Building Information System for Energy Efficiency & Comfort” project ((DGR Basilicata n. 15AB.2021.d.014333, CUP G49J19001400004), funded under the ERDF Operational Program 2014-2020 - Action 1B.1.2.2. "Public Notice" Complex Research and Development Projects "CORES" Thematic Areas "Energy and Bioeconomy". The authors are grateful to Dr. Annarita Renda, Emiliano Sicilia and Andrea Vennera of Scai Lab srl for the fruitful support in the measurement campaign during the project.

References

- [1] Neri, G. (2015) First Fifty Years of Chemosensitive Gas Sensors. *Chemosensors*, 3, 1–20.
- [2] Burratti, L.; Bolli, E.; Casalbani, M.; De Matteis, F.; Mochi, F.; Francini, R.; Casciardi, S.; Proposito, P. (2018) Synthesis of Fluorescent Ag Nanoclusters for Sensing and Imaging Applications. *Mater. Sci. Forum*, 941, 2243–2248
- [3] Cappelli, E., Bellucci, A., Medici, L., Mezzi, A., Kaciulis, S., Fumagalli, F., Di Fonzo, F. and Trucchi, D.M. (2015) Nano-crystalline Ag–PbTe thermoelectric thin films by a multi-target PLD system, *Applied Surface Science*, 336, 283-289.
- [4] Bellucci, A., Mastellone, M., Girolami, M., Orlando, S., Medici, L., Mezzi, A., Kaciulis, S., Polini, R. and Trucchi D.M. (2017) ZnSb-based thin films prepared by ns-PLD for thermoelectric applications. *Appl Surf Sci*, 418, 589-593.

- [5] Bellucci, A., Cappelli, E., Orlando, S. et al. (2014) Fs-pulsed laser deposition of PbTe and PbTe/Ag thermoelectric thin films. *Appl. Phys. A*, 117, 401–407.
- [6] Bellucci, A., Mastellone, M., Girolami, M., Serpente, V., Generosi, A., Paci, B., Mezzi, A., Kaciulis, S., Carducci, R., Polini, R., Orlando, S., Santagata, A., De Bonis, A., Meucci, M., Mercatelli, L., Sani, E. and Trucchi, D.M. (2020) Nanocrystalline lanthanum boride thin films by femtosecond pulsed laser deposition as efficient emitters in hybrid thermionic-photovoltaic energy converters. *Applied Surface Science*, 513, 145829.
- [7] Mezzi A, Soltani P, Kaciulis S, et al. (2018) Investigation of work function and chemical composition of thin films of borides and nitrides. *Surf Interface Anal.* 50, 1138–1144.
- [8] Bellucci, A., Sabbatella, G., Girolami, M., Mastellone, M., Serpente, V., Mezzi, A., Kaciulis, S., Paci, B., Generosi, A., Polini, R., Vitulano, A., Vivaldi, I., Antonelli, M. and Trucchi, D.M. (2021), Dielectric Micro- and Sub-Micrometric Spacers for High-Temperature Energy Converters. *Energy Technol.*, 9: 2000788.
- [9] Salerno, R., Valentini, V., Bolli, E., Mastellone, M., Serpente, V., Mezzi, A., Tortora, L., Colantoni, E., Bellucci, A., Polini, R. and Trucchi D.M. (2024) Low Electron Affinity Silicon/Nanocrystalline Diamond Heterostructures for Photon-Enhanced Thermionic Emission. *ACS Appl. Energy Mater*, 7, 3, 868–873.
- [10] Mezzi, A.; Bolli, E.; Kaciulis, S.; Bellucci, A.; Paci, B.; Generosi, A.; Mastellone, M.; Serpente, V.; Trucchi, D.M. (2023) Multi-Technique Approach for Work Function Exploration of Sc₂O₃ Thin Films. *Nanomaterials*, 13, 1430.
- [11] Bolli, E., Mezzi, A., Kaciulis, S., Serpente, V., Bellucci, A. and Trucchi, D.M. (2023) Temperature dependence of the work function in barium fluoride ultra-thin films on semiconductors for hybrid thermionic converters studied by ultraviolet photoelectron spectroscopy. *Surf Interface Anal*, 55(6-7), 541-547.
- [12] Bolli, E.; Fornari, A.; Bellucci, A.; Mastellone, M.; Valentini, V.; Mezzi, A.; Polini, R.; Santagata, A.; Trucchi, D.M. (2024) Room-Temperature O₃ Detection: Zero-Bias Sensors Based on ZnO Thin Films. *Crystals*, 14, 90.
- [13] Potyrailo, R.A. (2016) Multivariable sensors for ubiquitous monitoring of gases in the era of internet of things and industrial internet. *Chem. Rev.* 116, 19, 11877-11923. 2016.
- [14] Isaac, N.A., Pikaar, I. and Biskos, G. (2022) Metal oxide semiconducting nanomaterials for air quality gas sensors: Operating principles, performance, and synthesis techniques. *Mikrochim. Acta*, 189, 196.
- [15] Wang, Z., Bu, M., Hu, N., Zhao, L. (2023) An overview on room-temperature chemiresistor gas sensors based on 2D materials: Research status and challenge. *Compos. B Eng.* 248, 110378.
- [16] Song, Y.G., Kim, G.S., Ju, B.K. and Kang, C.Y. (2020) Design of Semiconducting Gas Sensors for Room-Temperature Operation, *J. Sens. Sci. Technol.* 29, 1-6.
- [17] Bellucci, A., De Bonis, A., Curcio, M., Santagata, A., Pace, M.L., Bolli, E., Mastellone, M., Polini, R., Salerno, R., Valentini, V. and Trucchi D.M. WO₃ thin films grown by pulsed laser deposition as gas sensors for NO₂ detection. Under review
- [18] Bolli, E., Bellucci, A., Mastellone, M., Mezzi, A., Orlando, S., Polini R., Salerno, R., Santagata, A., Valentini, V. and Trucchi D.M. (...) Engineered SnO₂-based thin films for efficient CO₂ gas sensing at room temperature. Submitted
- [19] Z. Wang, F. Wang, A. Hermawan, Y. Asakura, T. Hasegawa, H. Kumagai, H. Kato, M. Kakihan, J. Zhu, S. Yin, SnO-SnO₂ modified two-dimensional MXene Ti₃C₂T_x for acetone gas sensor working at room temperature, *J. Mater. Res. Technol.* 73 (2021) 128–138.
- [20] H. Yua, T. Yanga, Z. Wangc, Z. Lia, Q. Zhaoa, M. Zhang, p-N heterostructural sensor with SnO-SnO₂ for fast NO₂ sensing response properties at room temperature, *Sens. Actuators B.* 258 (2018) 517–526.
- [21] <https://scentroid.com/wp-content/uploads/2020/09/Scentroid-Sensor-list-V2.8.pdf>.