The GAMS 2024 International Conference

June 05 to 07 2024
Conference Proceedings

DOI:
https://doi.org/10.26799/cp-gams-2024

Proceedings of the GAMS 2024 International Conference
Paris, France – June 05 – 07, 2024
DOI: https://doi.org/10.26799/cp-gams-2024

Aerosol Assisted Chemical Vapor Deposition of Copper Sulfide films with sensitivity to NO_2

Houyem Trabelsi[1,2], Isabel Gràcia[2], Khaled Alouani[2], Stella Vallejos[1]

[1]Institute of Microelectronics of Barcelona (IMB-CNM, CSIC)
Universitat Autònoma de Barcelona
Campus, Carrer dels Til·lers, 08193, Barcelona, Spain, Houyem.Trabelsi@imb-cnm.csic.es
[2] Department of chemistry, University of Tunis El Manar, Faculty of Science
Foyer Universitaire, 20 Rue de Tolède, Tunis 2092, Tunis, Tunisia

Abstract

Metal chalcogenides (MC), such as copper sulfide (Cu_2S), have attracted significant interest among researchers due to their use in solar cells, gas sensing technology, and energy storage devices. Previous studies have explored the deposition of MC thin films employing physical or chemical methods. These approaches typically utilize a variety of precursors. However, single source precursor (SSPs) complexes offer advantages due to their simplified pathways for the MC synthesis. Hence, this works reports the synthesis of copper sulfide thin films (Cu_2S) from an experimental SSPs copper complex based on organochalcogenophosphorus ligand. The films were processed via Aerosol Assisted Chemical Vapor Deposition (AACVD) at 400 ºC and 450 ºC. SEM of the films demonstrated granular- or sheet-like morphology when deposited at 400 ºC or 450 ºC, respectively. EDX indicated a Cu/S ratio of 2 (anal. calc. for Cu_2S: Cu 39.9 and S 20.1 at%; found Cu 41.3 and S 20.6 at%). XRD results shows the films are crystalline and consistent with a tetragonal phase of Cu_2S (ICDD card nº 04-024-2237). Light activated test upon NO_2 showed better responses for the Cu_2S deposited at 450 ºC as compared to those deposited at 400 ºC.

Keywords: Copper Sulfide, Single Source Precursor, AACVD, Gas Sensors.

1. Introduction

Binary chalcogenide materials like SnS/Se, Cu_2S, ZnS and CdS/Se/Te have attracted the attention specially due to their optoelectronic and thermoelectric properties [1-3]. Previous studies have shown copper sulfides Cu_xS ($0<x<2$) as industrially significant materials due to their abundance, low cost, and a high performance at relatively elevated temperatures, which facilitate their uses in electronics [4], catalysis [5], photovoltaics [6], and energy storage [7], among other. Extensive research has also been performed on the use of these materials in the field of gas sensors, in order to detect and measure toxic, explosive, and volatile gases such as NO_2, NH_3, H_2S, CO_2, and several volatile organic compounds (VOCs) [8]. As examples, D Wang et al. demonstrated the selectivity performance of CuS flower-like sensor for ethanol gas against other interfering gases (methanol, dichloromethane, hexane and benzene) at low relatively temperature (170 ºC) and confirmed the stability of the sensor [9]. Additionally, Abhay and Ramphal showed that Cu_xS serve as sensor material for the detection of NH_3 molecules at room temperature [10].

In the state-of-the-art, different methods have been explored to deposit copper sulfide films including spray-pyrolysis [11], electrodeposition [12], chemical bath deposition [13], hydrothermal [14] and aerosol assisted chemical vapor deposition (AACVD) [15]. These approaches typically utilize a variety of precursors; among them single source precursor (SSPs) complexes, which offer advantages due to their simplified pathways for the metal chalcogenides synthesis. Indeed, SSPs complexes have been employed for the AACVD synthesis of copper sulphides, for instance dithiocarbamate $[Cu(S_2CNR_2)_2]_2$ [16] and bis(piperidinedithiocarbamato)copper(II) $[Cu(Ppdtc)_2]_2$ [17] with both SSPs having shown to successfully lead different structures and morphologies of Cu_xS at temperatures between 350ºC and 450ºC. Despite the adequacy of such a SPPs for AACVD, there is still a number of other organic ligands that can give rise to AACVD copper sulfide films with unexplored characteristics. Therefore, the motivation for investigating new copper complexes based on organochalcogenophosphorus ligands, such as the tetraethyldiphosphine disulfide ($Et_4P_2S_2$). Thus, the present report discusses the AACVD of copper sulfide (Cu_2S) thin films using the experimental $[Cu(Et_4P_2S_2)Cl]_2$ complex, and their structural, morphological, and gas sensing properties upon NO_2 as function of their deposition temperature.

DOI: https://doi.org/10.26799/cp-gams-2024

2. Experimental procedure

2.1 Deposition of copper sulfide (Cu_2S) thin films by AACVD

Copper sulfide films were deposited using the AACVD system reported early [18]. A schematic illustration of this system is displayed in Figure 1. Firstly, four silicon substrates (5 mm × 5 mm) were thoroughly cleaned by sonication in isopropanol for 10 min and dried under nitrogen to remove any possible contamination before placing them inside the AACVD reactor heated at the desire temperature (for this study, either 400 °C and 450 °C). Subsequently, we dissolved (in a two-necked round-bottom flask of 100 mL) 80 mg of the $[Cu(Et_4P_2S_2)Cl]_2$ complex in 10 ml of acetonitrile. An ultrasonic atomizer operating at 1.6 MHz was employed to transform the solution into fine aerosol droplets that were carried to the hot-wall reactor by a nitrogen flow of 200 sccm. The time to completely transport the solution into the reactor took typically one hour.

The samples were characterized by XRD, EDX, and SEM. The gas sensing properties of the microsensors were examined in a continuous gas flow systems equipped with calibrated gas bottles and mass flows to control the concentration of NO_2 (1, 3, 5 ppm) diluted in dry air. The system was also equipped with a chamber containing the microsensors and an UV-LED (365 nm) to excite the Cu_2S film and perform the photoactivated gas sensing tests at room temperature (25ºC).

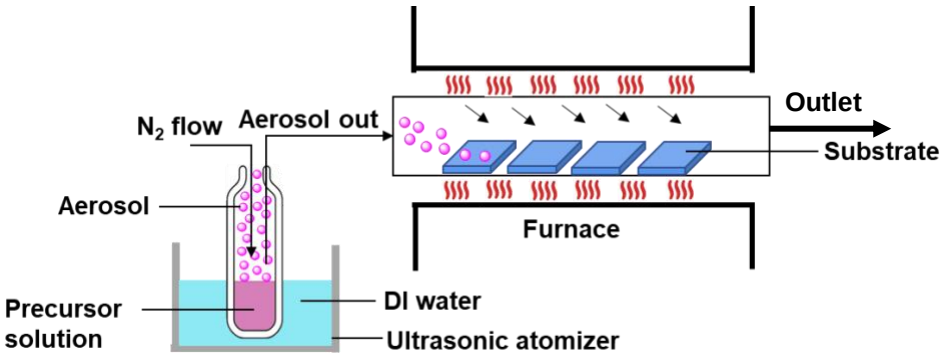

Figure 1. The schematic illustration of aerosol assisted chemical vapour deposition (AACVD) technique.

3. Results and discussion

The AACVD of $[Cu(Et_4P_2S_2)Cl]_2$ at 400 ºC and 450 ºC led to the deposition of black (at 400ºC) and brownish (at 400ºC) uniform films over the silicon tiles. The process was repeated several times for the two deposition temperatures studied finding good reproducibility of the results. The implementation of this process over silicon micromachined platforms for the fabrication of gas microsensor also lead to similar film characteristics. The sections below discuss the XRD, SEM, EDX recorded on the films and gas sensing results registered by the microsensors.

3.1 Thin film characterization

XRD analysis of the films deposited at 400 °C and 450 °C displayed patterns associated to a tetragonal phase of Cu_2S (ICDD card nº 04-024-2237), with a minor presence of phosphorus contamination reacting with the copper to form Cu_2P_7 phase (ICDD card nº 01-076-1189) (see Figure 2). For the sample obtained at 450ºC, an intense diffraction at 33º theta coming from the silicon substrate was also observed. EDX analysis also corroborated the formation of Cu_2S, indicating a Cu/S ratio of 2 (anal. calc. for Cu_2S: Cu 39.9 and S 20.1 at%; found Cu 41.3 and S 20.6 at%). Further analysis by SEM demonstrated the formation of granular- or sheet-like morphology films for the samples deposited at 400 ºC or 450 ºC, respectively (see Figure 3). Films with particle-like morphology, show small particles with size ranging from 60 nm to 100 nm, and agglomerated particles reaching around 400 nm. Further images of the cross-section of these films revealed a thickness of 1.3 µm. In contrast, the films with sheet-like morphology, displayed non-oriented and non-uniform sheet shapes with varied sizes between 3 to 10 µm. The cross section of these films showed a thickness between 20-22 µm.

DOI: https://doi.org/10.26799/cp-gams-2024

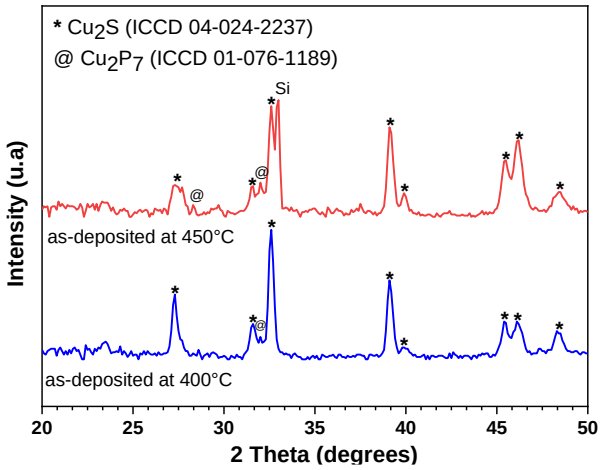

Figure 2. X-ray diffraction patterns of Cu_2S films deposited on Si substrates at 400°C and 450°C. The diffraction peaks in the data can be indexed to tetragonal Cu_2S and Cu_2P_7 phases, with only the peaks of greatly intensity marked by a start (*) and at symbol (@), respectively.

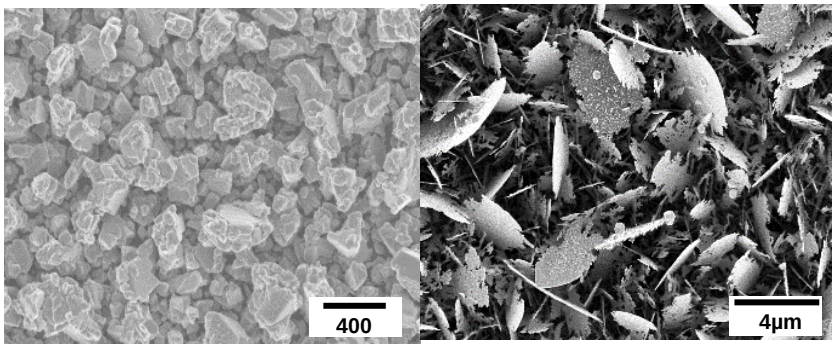

Figure 3. SEM images of Cu_2S thin films deposited at 400 ºC (left) and 450 ºC (right) on Si substrates.

3.2 Gas sensing properties

The Cu_2S based microsensors showed sensitivity to NO_2 under UV-light illumination. Specifically, results demonstrated that after the injection of NO_2 gas into the chamber, the electrical resistance of the particle and flake-like films increases significantly and proportionally to the gas concentration. This indicates an interaction of the NO_2 molecules with the Cu_2S surface. The tests showed the sensors exhibit stable and repeatable responses. Notably, the sensors based on flake structures demonstrated the highest responses to NO_2, most likely due to their greater surface area to volume ratio, as compared to the sensors based on films with particle-like morphology. The responses also showed to be reversible for both type of samples, registering faster response times for the flakes (60 s, for 5 ppm of NO_2) than for the particles (80 s, for 5 ppm of NO_2). A summary of these results is presented in Figure 4.

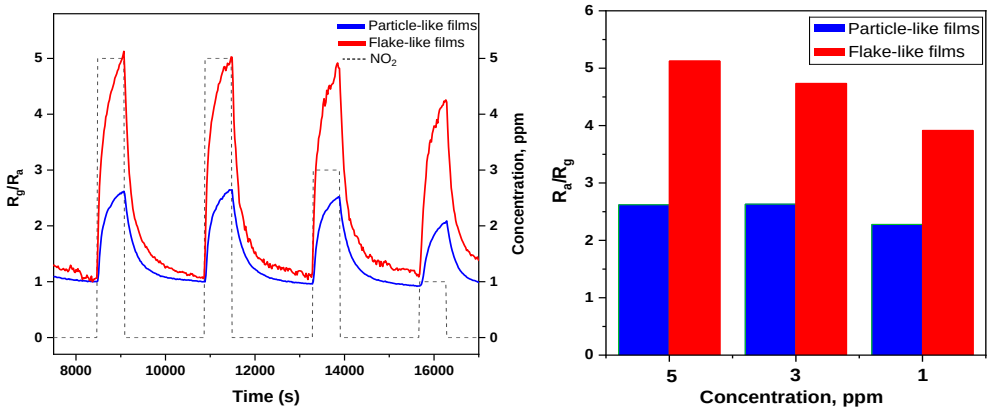

Figure 4. Light activated response of Cu_2S particle and flake based-sensors toward different concentration of NO_2 gas.

4. Conclusion

In summary, our study shows that the $[Cu(Et_4P_2S_2)Cl]_2$ complex acted as an effective single-source precursor for depositing Cu_2S films by AACVD technique. We found that the morphology of the resulting copper sulfide films strongly depends on the deposition temperature, with particles-like morphologies occurring at 400 ºC and flakes-like morphologies at 450 ºC. Evaluation, at room temperature, of the NO_2 response of the Cu_2S-based sensors activated by UV-LED indicate that flake-like sensors exhibit higher responses to this gas as well as faster response times (60 s) compared to particle-like sensors (80 s).

Acknowledgements

This work has been realized in the framework of the AGRARSENSE project supported by the Chips JU and the European Union (Grant agreement No. 101095835). The support of the Tunisian Ministry of Higher Education and Scientific Research (MHESR) is also acknowledged.

References

[1] M. W. Saleem, M. A. Rafiq, A. Hussain, and A. Javed, "Electronic, mechanical, dielectric and optical properties of cubic and orthorhombic tin monosulfide," *Materials Science in Semiconductor Processing*, vol. 144, p. 106616, Jun. 2022, doi: 10.1016/j.mssp.2022.106616.

[2] K. Assili, K. Alouani, and X. Vilanova, "Structural and optical properties of tin (II) sulfide thin films deposited using organophosphorus precursor (Ph_3PS)," *Semicond. Sci. Technol.*, vol. 32, no. 2, p. 025002, Feb. 2017, doi: 10.1088/1361-6641/32/2/025002.

[3] H. S. Ahmed and R. Y. Mohammed, "The Effect of Deposition Parameters on Morphological and Optical Properties of Cu2S Thin Films Grown by Chemical Bath Deposition Technique," *Photonics*, vol. 9, no. 3, p. 161, Mar. 2022, doi: 10.3390/photonics9030161.

[4] N. Aghad *et al.*, "Phase transition, structural, optical and thermoelectric properties of spin coated CuxS thin films," *Physica B: Condensed Matter*, vol. 673, p. 415506, Jan. 2024, doi: 10.1016/j.physb.2023.415506.

[5] A. Sudhaik *et al.*, "Copper sulfides based photocatalysts for degradation of environmental pollution hazards: A review on the recent catalyst design concepts and future perspectives," *Surfaces and Interfaces*, vol. 33, p. 102182, Oct. 2022, doi: 10.1016/j.surfin.2022.102182.

[6] M. Mousavi-Kamazani, Z. Zarghami, and M. Salavati-Niasari, "Facile and Novel Chemical Synthesis, Characterization, and Formation Mechanism of Copper Sulfide (Cu_2S, Cu_2S/CuS, CuS) Nanostructures for Increasing the Efficiency of Solar Cells," *J. Phys. Chem. C*, vol. 120, no. 4, pp. 2096–2108, Feb. 2016, doi: 10.1021/acs.jpcc.5b11566.

[7] Y. Quan *et al.*, "High-performance pseudo-capacitor energy storage device based on a hollow-structured copper sulfide nanoflower and carbon quantum dot nanocomposite," *Electrochimica Acta*, vol. 353, p. 136606, Sep. 2020, doi: 10.1016/j.electacta.2020.136606.

[8] R. K. Sonker, K. Singh, and R. Sonkawade, Eds., *Smart Nanostructure Materials and Sensor Technology*. Singapore: Springer Nature Singapore, 2022. doi: 10.1007/978-981-19-2685-3.

[9] D. Wang, M. Sun, G. Feng, and C. Song, "Ethanol Monitoring Gas Sensor Based on Flower-Shaped Copper Sulfide by a Facile Hydrothermal Method for Marine Transportation," *J. of Materi Eng and Perform*, vol. 28, no. 11, pp. 6649–6655, Nov. 2019, doi: 10.1007/s11665-019-04450-z.

[10] A. A. Sagade and R. Sharma, "Copper sulphide (CuxS) as an ammonia gas sensor working at room temperature," *Sensors and Actuators B: Chemical*, vol. 133, no. 1, pp. 135–143, Jul. 2008, doi: 10.1016/j.snb.2008.02.015.

[11] N. ArabHajji and H. Eshghi, "Study the effect of Cu to S molar ratios and annealing process on physical properties of CuxS thin films synthesized by spray pyrolysis method," *J Mater Sci: Mater Electron*, vol. 34, no. 24, p. 1731, Aug. 2023, doi: 10.1007/s10854-023-11173-4.

[12] A. Ait-karra *et al.*, "Electrodeposition and characterization of copper sulfide (CuS) thin film: towards an understanding of the growth mechanism," *J Solid State Electrochem*, vol. 27, no. 8, pp. 2051–2065, Aug. 2023, doi: 10.1007/s10008-023-05471-4.

[13] M. Chávez Portillo *et al.*, "Structural properties of sulfur copper (CuS) nanocrystals grown by chemical bath deposition," *Optik*, vol. 208, p. 164518, Apr. 2020, doi: 10.1016/j.ijleo.2020.164518.

[14] T. Marimuthu *et al.*, "Cost effective and facile low temperature hydrothermal fabrication of Cu2S thin films for hydrogen evolution reaction in seawater splitting," *International Journal of Hydrogen Energy*, vol. 47, no. 72, pp. 30819–30829, Aug. 2022, doi: 10.1016/j.ijhydene.2021.06.153.
[15] S. Saeed, N. Rashid, and K. S. Ahmad, "Aerosol-assisted chemical vapor deposition of copper sulfide nanostructured thin film from newly synthesized single-source precursor," *Turk J Chem*, vol. 37, pp. 796–804, 2013, doi: 10.3906/kim-1210-56.
[16] M. Kemmler, M. Lazell, P. O'Brien, D. J. Otway, J.-H. Park, and J. R. Walsh, "[No title found]," *Journal of Materials Science: Materials in Electronics*, vol. 13, no. 9, pp. 531–535, 2002, doi: 10.1023/A:1019665428255.
[17] M. D. Khan, M. Akhtar, M. A. Malik, N. Revaprasadu, and P. O'Brien, "New Examples of Phase Control in the Preparation of Copper Sulfide Nanoparticles and Deposition of Thin Films by AACVD from Bis(piperidinedithiocarbamato)copper(II) Complex," *ChemistrySelect*, vol. 3, no. 11, pp. 2943–2950, Mar. 2018, doi: 10.1002/slct.201703069.
[18] S. Vallejos, N. Pizúrová, J. Čechal, I. Gràcia, and C. Cané, "Aerosol-assisted Chemical Vapor Deposition of Metal Oxide Structures: Zinc Oxide Rods," *JoVE*, no. 127, p. 56127, Sep. 2017, doi: 10.3791/56127.