

Facile synthesis of SnS₂ nanosheets via the combination of AACVD and APCVD methods for ppb-level NO₂ detection

Aladine Fdhila^{1,2}, *Fatima Ezahra Annanouch*¹, *Zouhair Haddi*², *Eduard Llobet*¹

¹ *Departament d'Enginyeria Electronica, Universitat Rovira i Virgili, Països Catalans 26, 43007 Tarragona, Spain,*

² *NVISION Systems and Technologies, Avenida de Barcelona 105, 08700 Igualada, Barcelona, Spain*

Corresponding Author: eduard.llobet@urv.cat

Summary:

Tin disulfide (SnS₂) nanosheets, were successfully synthesized using the combination of aerosol assisted and atmospheric pressure chemical vapor deposition methods, (AACVD and APCVD). Morphological and compositional analysis demonstrated that this novel technique is suitable for producing high quality TMDs nanomaterials. By changing the sulfurization time (i.e. 30, 60 and 90 minutes), three different sensors, based on SnS₂ nanosheets, were fabricated and tested towards NO₂. The results showed that all the sensors were able to detect NO₂ at low operating temperature, while the highest response was recorded by sensor with 90 min of sulfurization.

Keywords: Gas sensors; SnS₂; TMDs; AACVD; APCVD; nanomaterials.

Background, Motivation an Objective

Two-dimensional (2D) materials, particularly transition metal dichalcogenides (TMDs), have attracted considerable interest due to their tunable bandgaps and exceptional electrical and optical characteristics. They offer a promising solution to common shortcomings (i.e., high operating temperature lack of selectivity) seen before in materials like carbon nanotubes, metal oxides, and graphene. Among TMDs, SnS₂ nanostructures exhibit ideal characteristics for gas sensing applications, including large surface area, rich in active reaction sites, high sensitivity to various gases, selectivity, stability, and reliability over prolonged use. However, SnS₂ synthesis faces some challenges. Various methods that have been used, such as hydrothermal synthesis and exfoliation techniques, have drawbacks like long reaction times, low yields, discontinuous films, environmentally unfriendly precursors and solvents etc. Herein, we introduce a novel way to successfully synthesize SnS₂ via the combination of AACVD and APCVD techniques. This approach allows us to directly deposit the TMDs on the sensor transducer, without the need of further transfer steps, improves the film quality and its long-term stability and resulted in highly sensitive and stable gas sensors.

Description of the New Method or System

The sensing films were directly grown on to alumina substrate, with Pt interdigitated elec-

trodes in the front side and a Pt resistive heater in the back side.

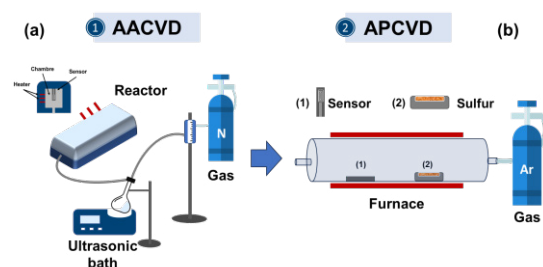


Fig. 1. (a) AACVD synthesis of SnO₂ nanostructures, and (b) APCVD synthesis of SnS₂ nanosheets.

Two steps of deposition were used to synthesize SnS₂: the first one (Fig.1 a), involved the direct growth of tin dioxide (SnO₂) nanostructures from the AACVD of 30 mg of tin(IV) chloride pentahydrate dissolved in 15 ml of acetone at temperature of 450°C. Herein, 0.5 L/ min of nitrogen, was used as a carrier gas. In the second step, the obtained SnO₂ nanostructures were subjected to an APCVD sulfurization process with argon serving as a carrier gas and sulfur powder (Fig.1 b). This process allowed the sensitive layer to grow directly at the alumina sensor transducer.

Results

First, we investigated the morphology of the SnO₂ nanostructures, displayed in Fig. 2 a, then the morphology of the produced SnS₂ nanosheets which is shown in Fig. 2 b. As we

can see, SnS₂ nanosheets were successfully grown with a perfect hexagonal shape, on top of the alumina substrate, using a straightforward combination of AACVD and APCVD techniques. We examined our sample using Raman spectroscopy in order to verify the composition and structure of SnO₂ and SnS₂. The Raman spectrum of SnO₂ (Fig. 2 c) is characterized by the classical vibrational band (A_{1g}) observed at 631 cm⁻¹ assigned to SnO₂ rutile structure. We also observed other peaks of 251 and 353 cm⁻¹ which can be assigned to optical phonon modes of SnO₂ (E_u (LO) and E_u (TO)) [1]. Regarding the SnS₂ spectrum (Fig. 2 d), we can see a sharp peak at 314 cm⁻¹ and a small one at 204 cm⁻¹ which are assigned to the vibrational modes (A_{1g}) and (E_g) of SnS₂ respectively [2]. All the finding confirmed the ability of our novel technique to produce SnS₂ from the direct sulfurization of SnO₂ nanostructures.

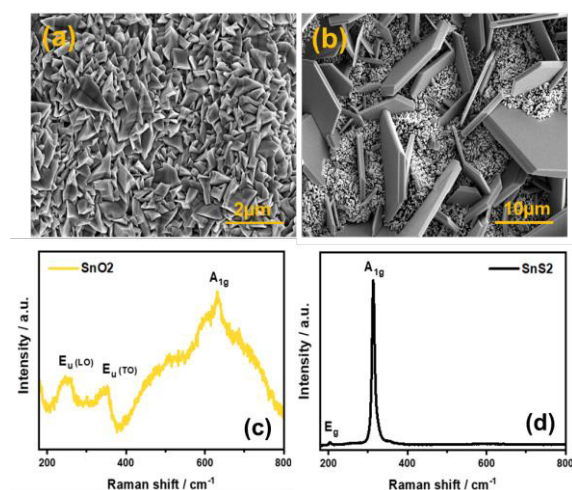


Fig. 2. FESEM images of (a) SnO₂, (b) SnS₂, and Raman spectra of (a) SnO₂, (b) SnS₂ nanostructures.

For gas sensing measurement, we fabricated three sensors with different sulfurization times (Sensor (A) 30 min; Sensor (B) 60 min; and Sensor (C) 90 min). The sensors were tested towards 500 ppb of NO₂, at different operating temperatures (RT, 50, 100, and 150°C), in order to study its effect on the sensor responses. From Fig. 3, we can observe that the optimal working temperature, for all the sensors, was 150°C, while the highest sensitivity was shown by sensors with 90 min of sulfurization. Besides, at room temperature, sensors (C) were able to detect the target gas at ppb-level, with enough sensitivity. Fig. 4 gives an example of the real sensor response as a function of time toward 500 ppb of NO₂ at 150°C. All sensors exhibited a p-type semiconductor behavior, decreasing resistance upon exposure to oxidizing gas and increasing it upon exposure to dry air.

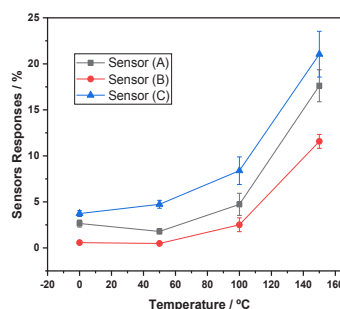


Fig. 3. Sensor responses toward 500 ppb of NO₂ as a function of temperature.

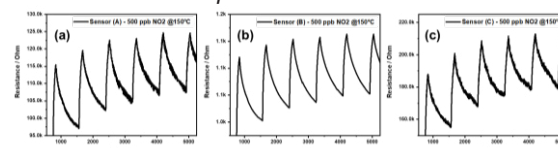


Fig. 4. Responses of SnS₂ gas sensors sulfurized for (a) 30min, (b) 60min, and (c) 90min, @150°C toward 500 ppb of NO₂.

Fig. 5 depicts the sensors responses as a function of NO₂ concentration. From the graph, the sensors responses increased by increasing the gas concentration, showing a linear behavior, which is very important parameter for real gas sensing application.

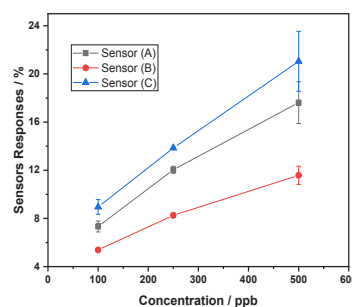


Fig. 5. Sensor responses toward NO₂ @ 150°C as a function of concentration.

Conclusions

This work reported a facile and scalable technique, to synthesize highly sensitive 2D hexagonal SnS₂ nanosheets, directly onto the sensor transducer, for the detection of ppb-level of NO₂ at low operating temperature. Details on humidity cross-reactivity will be shown at the conference.

References

- [1] T. Ahmad, M. Z. Ansari, Enhancement of infrared shielding property of SnO₂ using Sb as a dopant, *Materials Research Express* 10, 105902 (2022); doi: 10.1088/2053-1591/ac9778
- [2] Y. Ren, Q. Shi, G. Zhang, Lithium Storage Properties of TiC-Modified SnS₂ Nanosheets, *ChemElectroChem* 6, e202101567 (2022); doi: 10.1002/celec.202101567.