HIGHLY SENSITIVE H_2S GAS SENSOR BASED ON Ag AND Pt DECORATED SnO_2 THIN FILM

NGHIÊN CỨU CHẾ TẠO CẢM BIẾN KHÍ H_2S TRÊN CƠ SỞ MÀNG MỎNG OXIT THIẾC BIẾN TÍNH VỚI CÁC HẠT NANO BẠC VÀ PLATIN

Vo Thanh Duoc[1], Duong Thi Thuy Trang[1], Nguyen Van Toan[1], Lam Thi Hang[2], Bui Tien Trinh[2], Nguyen Si Hai[2], Vu Ngoc Phan[3,4], Phung Thi Hong Van[2*], Nguyen Van Duy[1*]

[1]International Training Institute for Materials Science, Hanoi University of Science and Technology

[2]Hanoi University of Natural Resources and Environment

[3]Phenikaa University Nano Institute, Phenikaa University

[4]Faculty of Biotechnology, Chemistry and Environmental, Phenikaa University

Đến Tòa soạn ngày 28/10/2021, chấp nhận đăng ngày 15/11/2021

Abstract: In this paper, we present the decoration of the SnO_2 film-based sensor with silver or platinum nanoparticles to enhance gas sensitivity to hydrogen sulfide gas (H_2S). Gas-sensitive properties and structure of fabricated sensors are investigated. It shows that the presence of Ag or Pt nanoparticles significantly improves the sensor sensitivity to H_2S. Among tested samples, the sensors decorated with nanoparticle layers of Ag (1 mm thick) or Pt (4 mm thick) have the best gas sensitivity at 250°C with H_2S gas concentration of 0.25 ppm.

Keywords: H_2S, gas sensor, SnO_2, thin film, nano.

Tóm tắt: Trong bài báo này, chúng tôi trình bày về việc biến tính cảm biến trên cơ sở màng SnO_2 với các hạt nano bạc hoặc platin nhằm tăng cường khả năng nhạy khí với khí hydro sulfua (H_2S). Các cảm biến chế tạo được được khảo sát tính chất nhạy khí, cấu trúc hình thái học. Kết quả nghiên cứu cho thấy sự có mặt của các hạt nano Ag hoặc Pt đều cải thiện đáng kể khả năng nhạy khí của cảm biến với H_2S. Trong đó các mẫu cảm biến biến tính với lớp hạt nano Ag (dày 1 mm) hay Pt (dày 4 mm) có khả năng nhạy khí tốt nhất ở 250 °C với nồng độ khí H_2S là 0,25 ppm.

Từ khóa: Cảm biến khí, SnO_2, H_2S, màng mỏng, nano.

1. INTRODUCTION

Hydrogen sulfide (H_2S) is a very toxic and flammable gas. Low concentrations of H_2S have a characteristic smell of rotten eggs [1]. The unpleasant odor is strong at low concentrations of about 5 ppm. At concentrations above 100 ppm, the gas quickly paralyzes the olfactory nerves. At low concentrations (50 ppm), H_2S irritates the eyes and entire respiratory tract. Prolonged exposure to 250 ppm causes alveolar membranes to secrete fluids that interfere with normal gas exchange. This causes the main symptom to suffocate and can lead to suffocation. Inhalation of high concentrations (1000 ppm) of H_2S will paralyze the respiratory nerve center, which can lead to suffocation. In addition to the effects of H_2S on the human body, the compounds of the fluid in the fuel gas will form SO_2 causing air pollution and human health problems [2].

Therefore, detection of H_2S gas at low, fast, and accurate concentration is very important.

Recently, studies focusing on developing sensitive, simple, inexpensive, and compact gas sensors to detect various gases have attracted significant attention. In which thin-film semiconductor metal oxide gas sensors have been researched, manufactured, and applied in many areas of life, they have many advantages such as high sensitivity, compact size, design. Simple, fast response time, low cost, and low power consumption. In many semiconductor metal oxides such as SnO_2, ZnO, TiO_2, WO_3... have been investigated as gas sensing materials [3]. SnO_2 materials have been extensively studied thanks to their unique properties and outstanding functions, which are widely applied in devices optoelectronic, biosensors, gas sensors, solar cells, etc. However, sensors based on SnO_2 membranes have poor selectivity, low sensitivity and operate at high temperatures [4]. Therefore, improving the gas sensor characteristics for a practical application requires high requirements. The denaturation of precious metals such as Pd, Pt, Ag, Au... including thin films, catalytic inversion positively affects the air-sensitive characteristics of the sensor. Studies have shown that Pt is a good catalyst that significantly enhances sensor performance [5–7]. S. Kolhe et al. [8] prepared Ag doped SnO_2 films were fabricated by using advanced chemical spray pyrolysis technique, showed the moderate response to H_2S gas and quick response time 0(~ 46 s) at 450 ppm. Wu et al. [9] reported that Ag-doped SnO_2 sensors measuring ethanol gas had a gas response of 2.24 and a short recovery-response time of 34 seconds and 68 seconds, respectively. Eom et al.[10] developed Pt/SnO_2 thin films by facile tilted sputtering process with hierarchical nanostructure enhanced H_2S gas response by a factor of 2 and the detection limit as low as 10 ppm compared to the thorough Pt loaded metal oxide at 150℃.

In the present work, the sensing SnO_2 thin film and the sensitizing SnO_2 thin film sensor activated with (Pt, Ag) are sequentially deposited by reactive sputtering without vacuum break and then patterned by photolithography. We describe the advanced response characteristics of Ag or Pt nanoparticles modified SnO_2-based sensors for H_2S gas.

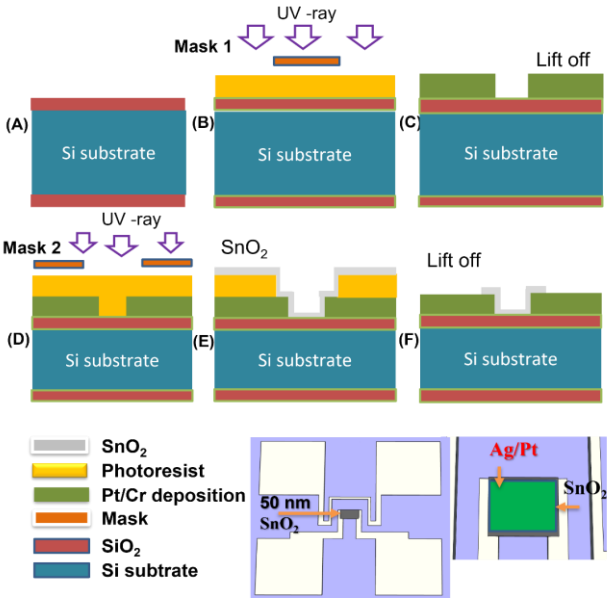

Figure 1. Process of realization of sensors by optical lithography and sputtering deposition. (A) SiO_2/Si/SiO_2 substrate; (B) Photolithography with the first mask and Cr/Pt metals sputtering; (C) Lift - off; (D) Photolithography with the second mask creates a window; (E) After sputtering the gas sensitivity material; (F) lift-off successful

2. EXPERIMENTAL

A pair of microheater and Pt electrodes composed of Cr (5nm) / Pt (100nm) layers were fabricated through the first mask coating and parallel sputtering deposition on SiO_2 / Si substrates. The thin-film structure of Pt / Ag /

SnO_2 was then deposited on the electrode by the sputtering method after the second mask alignment. The SnO_2 material was prepared by sputtering with Ar / O_2 flow rate (2: 1), sputtering capacity is 30 W. Electrodes and other catalyst materials were prepared at 80 W dc and Ar gas flow. The manufacturing process is shown in Figure 1. In this article, the film thickness was about 75 nm. There are seven fabricated sensors including a pure SnO_2, three Pt nanoparticle decorated SnO_2 thin-films (denoted as P2, P4 and P8); and three Ag nanoparticle decorated SnO_2 thin-film (denoted as A1, A2 and A4). The manufacturing parameters of these sensors are given in Table 1. All the samples were heat treated at 500 °C to stabilize the nanomaterial and improve its sensor performance. Morphology, structure, and composition of the thin films were investigated through scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersion spectroscopy (EDS).

Table 1. Prepared sensor samples, the name of which reflects the materials used and their thickness

No.	Material/ Catalyst	Sputtering time (s)	Thickness (nm)	Sample name
1	SnO_2	420	50	SnO_2
2	Pt	30	2	P2
3	Pt	60	4	P4
4	Pt	120	8	P8
5	Ag	20	1	A1
6	Ag	40	2	A2
7	Ag	80	4	A4

3. RESULTS AND DISCUSSION

The gas sensing characteristics of bare SnO_2 and A1-A2-A4, P2-P4-P8 were measured to explain the effectiveness of SnO_2 / Ag / Pt membrane sensitivity. First, we evaluated the H_2S gas sensor performance of the SnO_2 sensor. The gas sensing properties of bare SnO_2 nanofilm sensors at different temperatures (200, 250, 300 and 350 °C) and concentration of H_2S gas (0.25, 0.5, 1, 2.5 ppm) are shown in Figure 2 (A). The SnO_2 sensor shows almost 100 % resilience at all measured temperatures (Figure 2), showing the reversible adsorption of H_2S molecules on the sensor surface. In Figure 2 (B) shows that at 300 °C, the optimal temperature of Ag modified SnO_2 sensors at the concentration of 2.5 ppm H_2S gas, in which the thicker the Ag sensor, the more sensitive the sensor. The A4 sensor is more sensitive than the rest of the sensors. However, the recovery response time also increased with the thickness of Ag layer (shown in Table 1), so for the best results we chose Ag investigation conditions at thickness A1. As for the Pt transducer SnO_2 sensor in Figure 2 (C), the results show that the P4 sensor is a more sensitive sensor than the other 2 sensors at a temperature of 250°C, at 2.5 ppm H_2S.

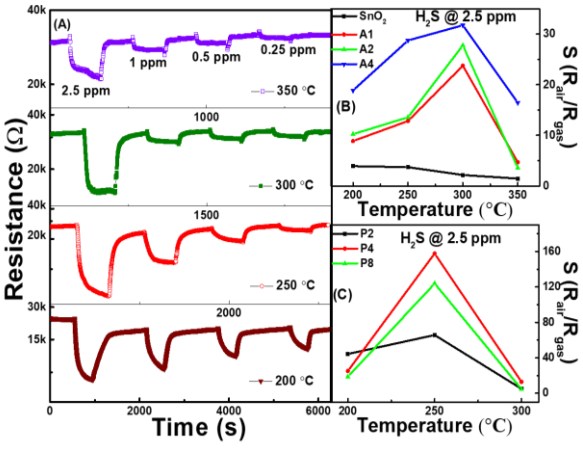

Figure 2. (A) Dynamic resistance of the pure-SnO_2 sensor at different temperatures, in response to the injection of different concentrations of hydrogen sulfide; (B) Comparison graph of modified SnO_2 sensors Ag at different temperatures at the concentration of 2.5 ppm; (C) Comparison graph of modified SnO_2 sensors Pt at different temperatures at the concentration of 2.5 ppm

The thin-film sensors were observed through the SEM image from Figure 3 (A-D). The SnO_2 surface was made of nanoparticles a size of approximately 30 nm (Figure 3A). The SnO_2 film thickness was fixed in samples of about 75 nm (Figure 3B). The modified P4 sample was evenly distributed on the surface of SnO_2 (Figure 3C). Ag nanoparticles are unevenly distributed on the SnO_2 membrane (Figure 3D). We suggest that the P4 model will exhibit good gas sensing properties because the particles are evenly distributed.

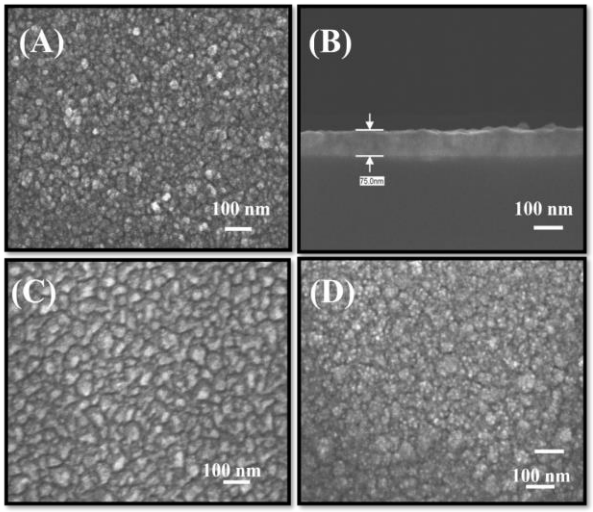

Figure 3. SEM images of thin films used as sensors. A) and B) pure SnO_2 (top view and cross section); C) P4 sample, D) A1 samples.

The structure of the films has been studied through XRD, whose patterns are shown in Fig. 3A. At the bottom, the black pattern is relative to pure SnO_2 and shows 2 peaks at angles of 34.0 and 51.9°, corresponding to the planes (101) and (211) of the rutile structure of SnO_2, respectively. In the pattern at the top (sample P4), two additional peaks at 39.7 and 46.2° can be seen, indexed in green as (111) and (200) planes of Pt, respectively, according to the JCPDS card 65-2868. Conversely, the presence of Ag in the second (red) pattern from sample A1 is not evident, probably because of the small amount of the decorating silver. The composition of SnO_2, P4, A1 sensor films analyzed by EDX showed the existence of Sn, Pt, Ag and O (Figure 4B-C). According to the spectrum, the ratio of Pt atoms in the sample P4 was approximately 2.6 %, the ratio of Ag in samples (A1) was approximately 2.9 %. The composition and content of Ag and Pt in films are difficult to determine due to the highly dispersed SiO_2 / Si substrate.

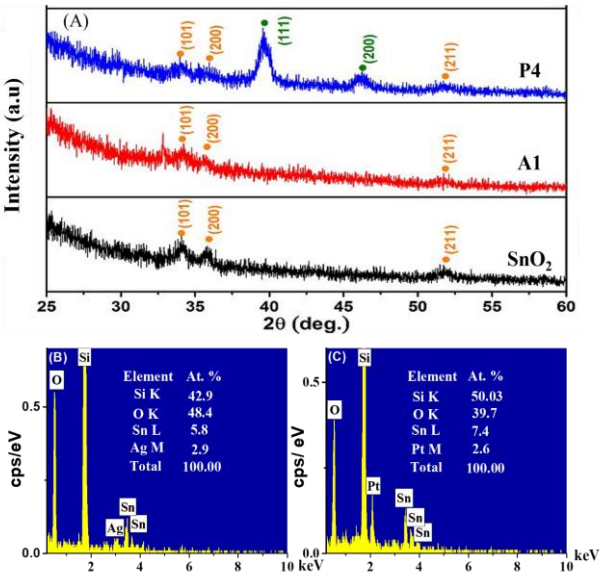

Figure 4. (A) XRD patterns of the SnO_2, A1, P4 sensing films and (B, C) EDS spectrum from the A1 and P4 sensor

4. CONCLUSION

Gas sensors based on SnO_2 semiconductor metal oxide thin films decorated with Pt or Ag metal particles have been studied and compared with pure SnO_2 sensors. Decorating with metal catalysts always improves the performance of the sensor. Both the decorative Pt and Ag on the SnO_2 film have the effect of increasing the sensor's performance compared to the pure SnO_2 sensor. The best performance is obtained with sensors based on SnO_2 membranes decorated with either Ag (1 nm) or Pt (4 nm) working at

250°C. The sensor has a good response at low concentrations of 0.25 ppm H_2S gas. These results make it an ideal candidate for practical applications.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Natural Resourses and Environment under the Grant No. TNMT.2018.04.14.

REFERENCES

[1] A. Mirzaei, S.S. Kim, H.W. Kim, "Resistance-based H_2S gas sensors using metal oxide nanostructures: A review of recent advances", J. Hazard. Mater. 357 (2018) 314–331.

[2] G. Huang, E. He, Z. Wang, H. Fan, J. Shangguan, E. Croiset, Z. Chen, "Synthesis and Characterization of γ-Fe_2O_3 for H_2S Removal at Low Temperature", Ind. Eng. Chem. Res. 54 (2015) 8469–8478.

[3] A. Ghosh, C. Zhang, S. Shi, H. Zhang, "High temperature CO_2 sensing and its cross-sensitivity towards H_2 and CO gas using calcium doped ZnO thin film coated langasite SAW sensor", Sensors Actuators, B Chem. 301 (2019) 126958.

[4] A. Staerz, T. Suzuki, U. Weimar, N. Barsan, "SnO_2: The most important base material for semiconducting metal oxide-based materials", Elsevier Inc., 2020.

[5] N.X. Thai, N. Van Duy, N. Van Toan, C.M. Hung, N. Van Hieu, N.D. Hoa, "Effective monitoring and classification of hydrogen and ammonia gases with a bilayer Pt/SnO_2 thin film sensor", Int. J. Hydrogen Energy. 45 (2020) 2418–2428.

[6] M. Shahabuddin, A. Sharma, J. Kumar, M. Tomar, A. Umar, V. Gupta, "Metal clusters activated SnO_2 thin film for low level detection of NH_3 gas", Sensors Actuators, B Chem. 194 (2014) 410–418.

[7] S. Das, V. Jayaraman, "SnO_2: A comprehensive review on structures and gas sensors", Prog. Mater. Sci. 66 (2014) 112–255.

[8] P.S. Kolhe, P.M. Koinkar, N. Maiti, K.M. Sonawane, "Synthesis of Ag doped SnO_2 thin films for the evaluation of H_2S gas sensing properties", Phys. B Condens. Matter. 524 (2017) 90–96.

[9] Z. Zhu, C.T. Kao, R.J. Wu, "A highly sensitive ethanol sensor based on Ag@TiO_2 nanoparticles at room temperature", Appl. Surf. Sci. 320 (2014) 348–355.

[10] N.S.A. Eom, H. Cho, H. Lim, B.S. Kim, Y. Choa, "Facile tilted sputtering process (TSP) for enhanced H_2S gas response over selectively loading Pt nanoparticles on SnO_2 thin Films", Sensors Actuators B. Chem. (2019) 127009.

Thông tin liên hệ: **Phùng Thị Hồng Vân**

Điện thoại: 0983168699 - Email: pthvan@hunre.edu.vn
Khoa Khoa học cơ bản, Trường Đại học Tài nguyên và Môi trường Hà Nội

Nguyễn Văn Duy

Điện thoại: 0985897027 - Email: duy.nguyenvan@hust.edu.vn
Viện Đào tạo Quốc tế về Khoa học vật liệu, Trường Đại học Bách khoa Hà Nội.