DEPOSITION AND STUDY OF ALCOHOL VAPOR SENSITIVITY OF $SnO_2/ZnSnO_3$ THIN FILMS

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Abstract: *The thin films of $SnO_2/ZnSnO_3$ were deposited on glass wafer substrate by a compression sprayer deposition system using $Zn(CH_3COO)_2.2H_2O$ and $SnCl_4.5H_2O$ as precursors. The surface of the films were treated in HCl acid solution 2% to improve their surface porosity. The influence of the surface treatment time, working temperature and alcohol vapor concentration on the sensitivity properties of the films were investigated. SEM images showed that the films treated for 60 min exhibited the best surface porosity. The phase analysis showed the presence of SnO_2 and $ZnSnO_3$ crystal phase on the films. The surface porosity, working temperature and alcohol concentration influenced strongly on the sensitivity properties of the films. The films with high surface porosity showed high sensitivity. The best sensitivity of the films was found on the films treated in HCl solution for 60min.*

Keywords: *$SnO_2/ZnSnO_3$ thin films, alcohol sensor, surface porosity, surface treatment*

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1. INTRODUCTION

Gas sensors have been developed for a long time and have contributed significantly to protecting the environment. Indeed, gas sensors have been used to detect hazards including carbon monoxide, harmful industrial solvents, and explosives [1, 2]. Currently, the materials commonly used for sensors are semiconductor metal oxides such as: SnO_2, ZnO, In_2O_3, WO_3, TiO_2, ABO_3... [3-7] due to their sensitivity to many dangerous gases or vapours. Among them, SnO_2 is a low cost material and has physicochemical properties suitable for

sensor applications. Therefore, it has particularly been attracting the attention of researchers, both private investigator and government researchers and policy makers as well.

Recently, the $ZnSnO_3$ material has also attracted wide attention because it is sensitive to certain toxic gases [8-11]. The combination of SnO_2 and $ZnSnO_3$ is expected to bring a lot of potential for applications in multi-system sensors [12,13].

Although the gas sensors have been extensively studied and commercialized the need to improve sensitivity and selectivity with different gases remains a challenge [14]. Current trend to solve these problems is to find out the fabrication process to reducing particle size, dope suitable element, improve the surface contact area and increase the surface porosity of samples [15].

In this study, the surface of $SnO_2/ZnSnO_3$ thin films were modified by treating samples in hydrochloric acid solution for incresing their surface porosity to improve their sensitivity to alcohol. This idea stems from the fact that SnO_2 is corroded in HCl very weakly compared to $ZnSnO_3$. Different corrosion rates of the elements in the samples will change its surface morphology and create holes on it. This process increases the surface porosity of sample, resulting in increasing its gas sensitive.

2. CONTENT

2.1. Experimental

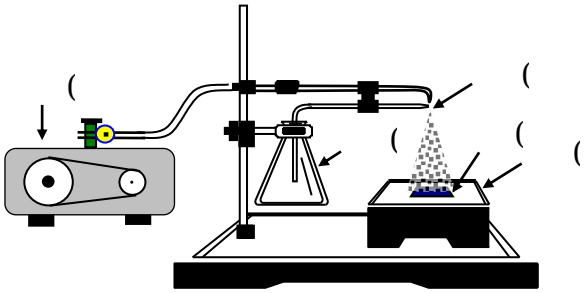


Fig 1: *Schematic diagram of the experimental apparatus: (1)-Compressor, (2)-Spray nozzle, (3)-Solution tank, (4)-Heater, (5) glass wafer*

Thin films of $SnO_2/ZnSnO_3$ were deposited by spray pyrolysis method. Figure 1 shows the schematic diagram of the spray system. Spray solution is prepared by dissolving $Zn(CH_3COO)_2.2H_2O$ and $SnCl_4.5H_2O$ in a solution containing 50% alcohol and 50% distilled water. The solution is then sprayed on the hot substrate at different temperatures by a compress sprayer. The chemical reactions under heat have created $SnO_2/ZnSnO_3$ film. Deposition parameters such as deposition temperature, solution concentration and spraying

rate are carefully determined to find the optimum condition to deposit films. The best quality of films is selected for surface treatment by immersing the films in hydrochloric acid solution 2%. The crystal structure of the material was studied by X-ray diffractometer (D8 ADVANCE BRUCKER) with Cu Kα radiation (λ = 0.154056nm). Surface morphology is observed by SEM (HitachiS-4800). Alcohol vapors sensitivity is investigated by a homemade system in which the resistance is measured by a Keithley 2000 multi-meter via a time versus resistance measurement program.

2.2. Result and discussion

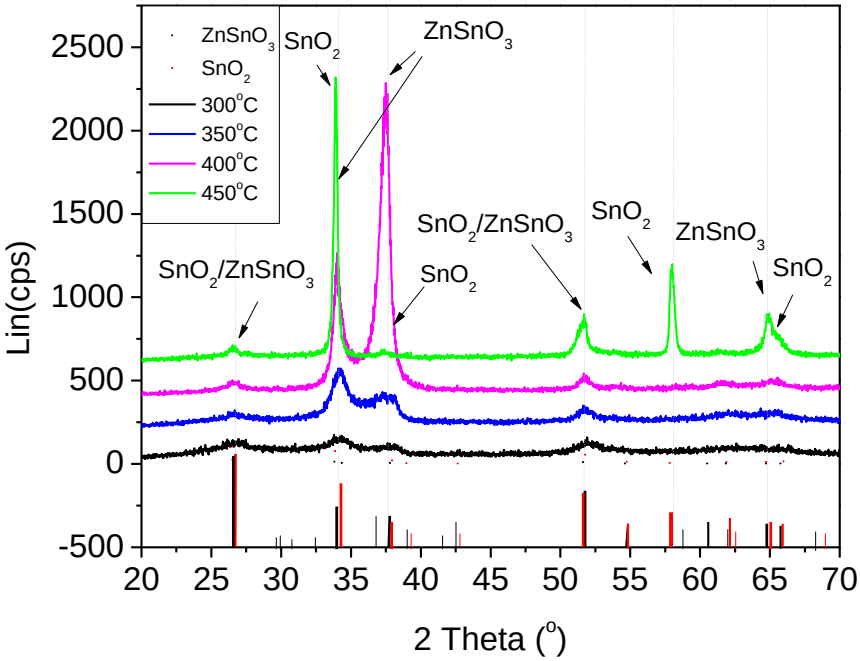


Fig. 2: *The X-ray difraction patterns of $SnO_2/ZnSnO_3$ thin films deposited with different temperature*

$SnO_2/ZnSnO_3$ thin films was deposited on the glass wafer by pressure spray method at different temperatures. Fig. 2 shows the X-ray diffraction patterns of the samples. The red lines correspond to the diffraction peaks positions of SnO_2 and the black lines correspond to the diffraction peaks positions of $ZnSnO_3$.

The diffraction patterns show the presents of crystal phases of SnO_2 and $ZnSnO_3$ corresponding to the tetragonal structural (refer to JCPDS No. 41-1445) and perovskite structural (refer to JCPDS No. 28-1486), respectively. No diffraction peaks of any other impurities were found. The intensity of diffraction peaks is increased with the increase in deposition temperature. This indicates that the films were crystallized better at high

temperature. However, the full width at half maximum peaks gradually decreased with deposition temperature indicating that grain size was increased.

Fig. 3 shows the X-ray diffraction patterns of samples treated in hydrochloric acid solution with different time: 0 minutes, 40 minutes, 60 minutes and 120 minutes. The diffraction peaks of SnO_2 and $ZnSnO_3$ are marked by red lines and blue lines, respectively.

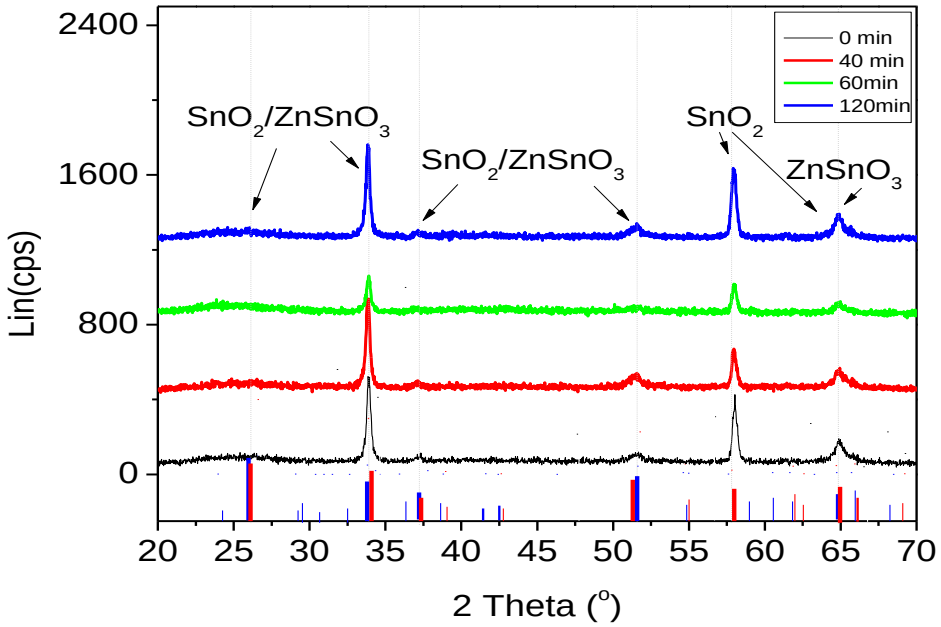


Fig. 3: *The X-ray difraction patterns of $SnO_2/ZnSnO_3$ thin films treated in HCl solution with different time*

The diffraction patterns show that there are no changes in structure compared to the original samples. Thus, hydrochloric acid mainly modified the surface without causing reactions inside the films.

Figure 4 is the SEM images of $SnO_2/ZnSnO_3$ films with and without a surface treatment. Analysis results showed that the surface morphology of the films changed after treatment.

The untreated sample has a quite smooth surface while the treated sample for 40 minutes has left crystals with sharp edges on the surface. Increasing treatment time to 60 minutes, crystals tend to be corroded more and the edge shape no longer observed. The ratio of the specific surface area to the particle volume has been increased with the increase in treatment time. Further increasing the treatment time to 120 minutes, the rough parts on the surface of the films are corroded more strongly and removed from the surface leading to smooth films.

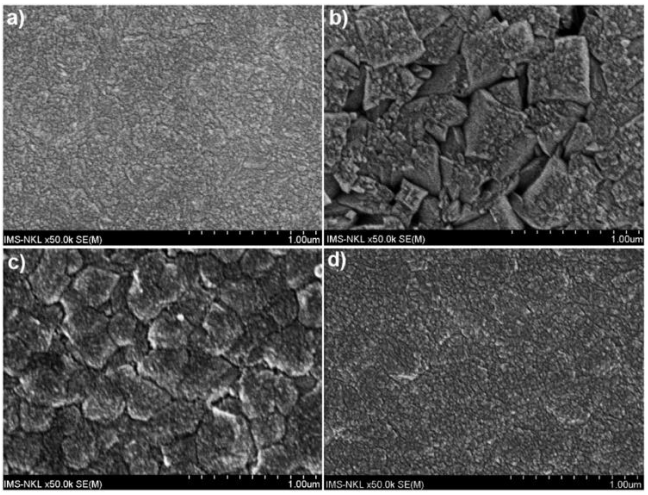
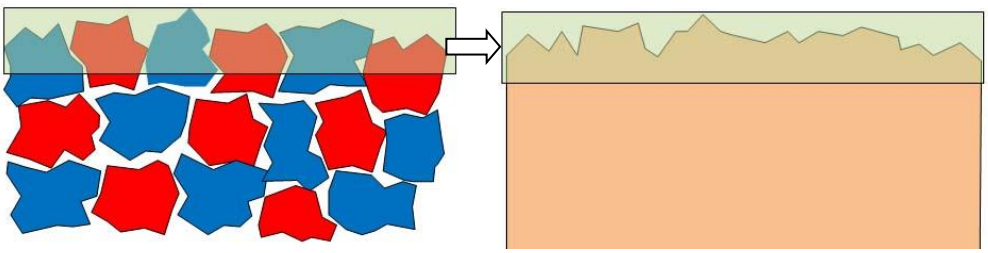


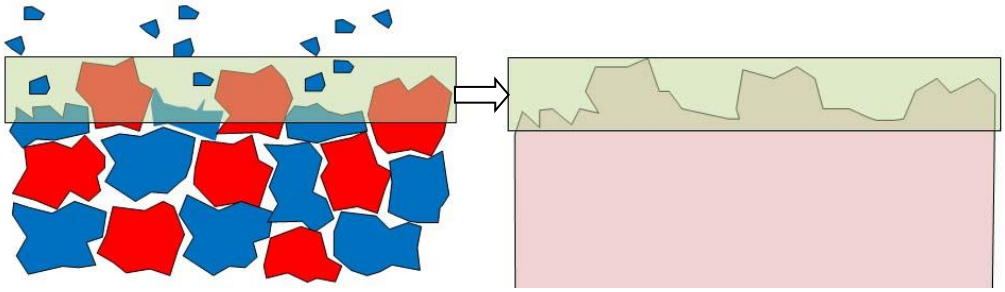
Fig. 4: *The SEM images of $SnO_2/ZnSnO_3$ thin films treated in HCl solution with different time: a)-0 min, b)-20 min, c)-60 min, d)-120 min*

The quantitative calculation of the porosity of the film by "Origin" software also showed that the surface porosity of the treated samples is higher than that of untreated one. The largest surface porosity was found on the sample treated for 60 minutes.

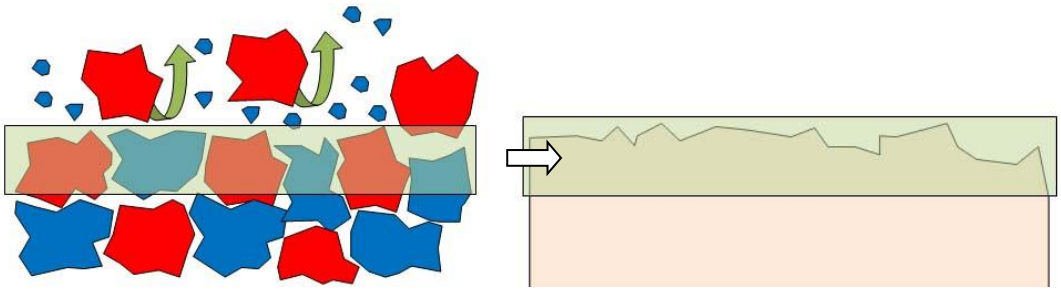
The modification of surface are explained by the corrosive process as following model:



a) The sample without corrosion



b) The sample is correded in short time



c) The sample is corroded in long time

Fig. 5: *The acid corrosion process of sample*

The sample consist of SnO_2 and $ZnSnO_3$ particles that are arranged alternately shown in Figure 5 a (SnO_2 particles are red, $ZnSnO_3$ is blue). Because of the faster corrosion rate of $ZnSnO_3$, the $ZnSnO_3$ crystalline particles are corroded first and leave holes on the surface (Figure 5b). If the surface is treated for a short time the holes will remain on the surface. Increasing the treatment time, the $ZnSnO_3$ around SnO_2 can be corroded completely so that SnO_2 is easy to removed from the surface. The surface becomes flat (Figure c).

The alcohol sensitivity of samples was determined as following: The sensitivity of untreated samples to alcohol versus temperature was determined first to fine optimum working temperature of sensor. The sensitivity of treated samples will then be investigated at this optimal temperature.

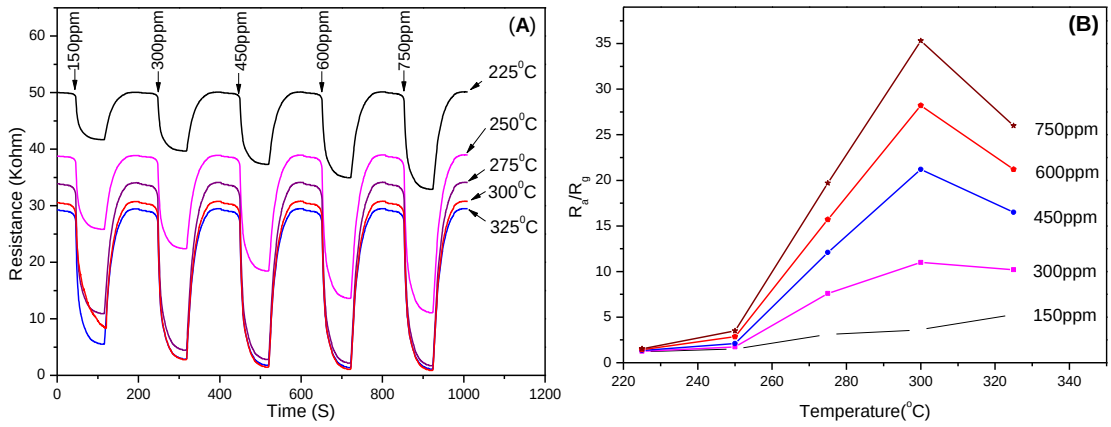


Fig. 6*. The ability of alcohol sensitivity of untreated samples with different temperatures: (A)-resistance vs. time, (B)- resistance response*

Fig. 6 shows the effect of the temperatures on the resistance response of the untreated samples. The results showed that the operating temperature of the sensor strongly affects the alcohol sensitivity ability of the films. The alcohol vapor sensitivity increases with the

increase of temperature in the temperature range below 300°C. Further increasing temperatures, the sensitivity decreases. The gas sensitivity is strongly influenced by the adsorption temperature and oxygen concentration on the grain boundary. As the temperature increases, the reactions between the gas and the adsorbed oxygen increase leading to increased gas sensitivity. Along with the above process, the increase in temperature speed up the desorption process, resulting in decreasing the adsorption oxygen concentration. This process decreases the sensitivity. Thus, at the same time, two opposite processes occur. The rule of increasing or decreasing the sensitivity will depend on which process is dominant. At temperatures lower than 300^{o}C, the reactions with adsorbed oxygen process is dominant, so the sensitivity increases with temperature. At temperatures higher than 300^{o}C, the desorption process is dominant, so the sensitivity decreases with temperature. In this study, the sensitivity of films reaches the optimum value at 300^{o}C.

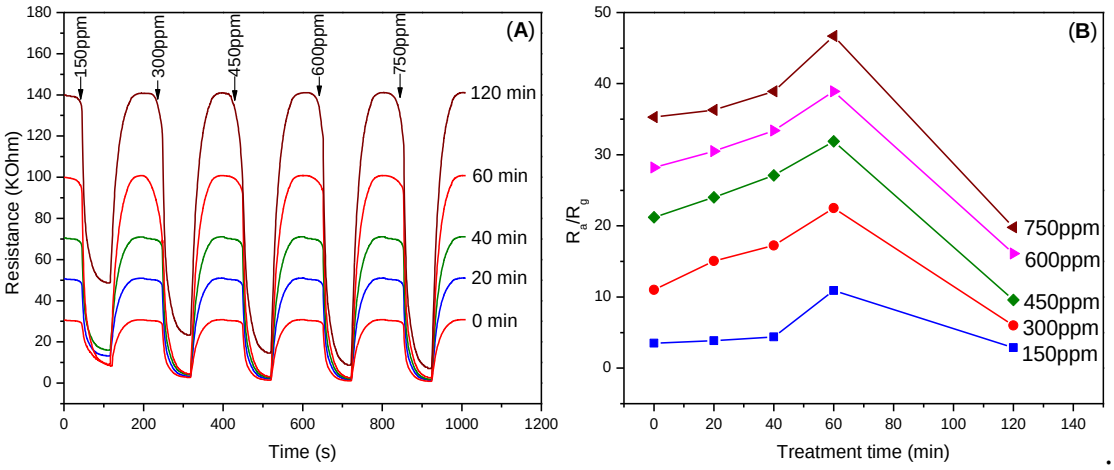


Fig. 7*. The ability of alcohol sensitivity of samples with different time treatment: (A)-resistance vs. time, (B)- resistance response*

In recent publication [16], the sensitivity of the $SnO_2/ZnSnO_3$ films increased with the increase of alcohol concentration up to 200ppm. Above 200ppm, the sensitivity of films increases slightly to approach saturation value. Meanwhile, the $SnO_2/ZnSnO_3$ in this study showed that the sensitivity value increases with increasing alcohol concentration. This means that the sensitivity of the films has not reached the saturation value and sensitivity range of this films is expanded.

The effect of the surface treatment time on the alcohol sensitivity of films was investigated at the optimum temperature (300^{o}C). Fig. 7 shows the effect of surface treatment time on the alcohol sensitivity with alcohol concentrations of 150 ppm, 300 ppm, 450 ppm, 600 ppm and 750 ppm. The alcohol vapor sensitivity of the samples increased with the

surface treatment of the samples from 0 minutes to 60 minutes. Further increase of treatment time, the sensitivity is decreased. The change in sensitivity over the treatment time is the result of the surface modifications process. Indeed, the samples have high sensitivity are those has high surface porosity because the improvement of specific surface area promotes chemical reactions on the surface of samples.

3. CONCLUSION

Thin films of $SnO_2/ZnSnO_3$ were successfully deposited by the pressure spray method. The surface of samples can be modified by treating with HCl solution 2% to improve the surface porosity of samples. The samples treated for 60 min have highest surface porosity. The films exhibit good sensitive to alcohol vapour. The films can detect alcohol with the concentration of 150 ppm. The optimum working temperature of films is 300^oC. The film modification by surface treatment improves the alcohol sensitivity of the films. The film treated for 60 min shows the best sensitivity.

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CHẾ TẠO VÀ NGHIÊN CỨU TÍNH CHẤT NHẠY HƠI CỒN CỦA MÀNG MỎNG $SnO_2/ZnSnO_3$

Tóm tắt: *Màng mỏng $SnO_2/ZnSnO_3$ phủ trên đế kính đã được chế tạo thành công bằng phương pháp phun áp suất từ dung dịch ban đầu là $Zn(CH_3COO)_2.2H_2O$ và $SnCl_4.5H_2O$. Bề mặt của màng mỏng được xử lý trong dung dịch a xít HCl 2% nhằm cải thiện độ xốp bề mặt của chúng. Ảnh hưởng của thời gian xử lý bề mặt, nhiệt độ làm việc của màng, và nồng độ hơi cồn lên tính chất nhạy hơi cồn của màng đã được nghiên cứu kỹ lưỡng. Ảnh SEM cho thấy những màng được xử lý trong a xít HCl 2% trong 60 phút cho độ xốp bề mặt tốt nhất. Các phép phân tích pha cấu trúc tinh thể cho thấy có sự xuất hiện của hai pha tinh thể SnO_2 và $ZnSnO_3$ trong màng mỏng. Độ xốp bề mặt, nhiệt độ môi trường đo mẫu và nồng độ hơi cồn ảnh hưởng mạnh mẽ lên tính nhạy hơi cồn của màng. Màng có độ xốp cao sẽ có độ nhạy hơi cồn lớn. Màng được xử lý trong a xít với thời gian 60 phút có khả năng nhạy hơi cồn tốt nhất.*

Từ khóa: *Màng mỏng $SnO_2/ZnSnO_3$, cảm biến nhạy hơi cồn, độ xốp bề mặt, xử lý bề mặt.*