THE DEPOSITION OF Zn-DOPED SnO_2 THIN FILMS BY A COMPRESSION SPRAYER FOR ALCOHOL VAPOR SENSOR

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***Abstract**: The thin films of SnO_2 and Zn-doped SnO_2 were deposited on glass wafer substrate by a compression sprayer system using $SnCl_2.2H_2O$ and $Zn(CH_3COO)_2.2H_2O$ as precursors. The influence of the deposition temperature and Zn-doped contents on SnO_2 and Zn-doped SnO_2 crystal phase were investigated by XRD, respectively. The results showed that the films of SnO_2 start to crystallize in the form of tetragonal structural at temperature of 370^oC. SnO_2 films were crystalized well at temperature above 400^oC. SnO_2 still retained the crystal structure when the Zn impurity content was up to 2%. Further increasing in Zn content, the films had more crystalline phases of zinc oxide. The surface morphology of the films observed by SEM showed that the shape of the SnO_2 crystals with size less than 100nm was fairly uniformly. The crystal size decreased slightly with increasing impurity content. The impurities influenced greatly on the alcohol vapor sensitivity of the films. The sensitivity of pure films increased with an increase in operation temperature even in high temperature. The sensitivity of the Zn-doped films increases with the increase in operation temperature up to 350^oC. Further increase in temperature decreases the sensitivity. At the optimum operation temperature, the films with 2 % Zn showed the best sensitivity.*

***Keywords**: SnO_2, Zn-doped SnO_2, alcohol sensitivity, compression sprayer.*

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1. INTRODUCTION

Organic solvents including ethanol, methanol, acetone… are *potential hazards to human health*. They have the ability to stimulate nerves, cause dizziness, headaches and even lose the ability to control behavior [1]. Unfortunately, these chemicals are commonly used in industrial processes where a large number of workers are working. Besides, drinking alcoholic beverages can impact the driving ability of driver, causing an accident or traffic insecurity. It is necessary to have highly sensitive sensors to detect the solvent vapors in the air and measure the

concentration of alcohol in the breath. Gas sensors based on semiconductor metal oxide (SMO) thin films such as SnO_2, ZnO, TiO_2, Fe_2O_3 and WO_3… are well suited for this purpose due to their ability to change resistance upon interaction with toxic gases [2, 3, 4**,** 5]. Among the SMOs, SnO_2 that has good chemical stability and stably in high temperature conditions has been widely used for gas sensor. Because of oxygen vacancies, SnO_2 is an n-type semiconductor and it donates electrons to other element in most reaction process [6, 7]. In air, oxygen will take electrons from SnO_2 to become adsorbed oxygen on the surface, resulting in an increase in the resistance of the film. Organic vapors are usually reducing agents so that they can react with the adsorbed oxygen and return the electrons to SnO_2, causing the decrease of its electrical resistance. Thanks to this property, SnO_2 thin films can be used as organic vapor sensitive sensors [8]. However, pure SnO_2 usually gives low selectivity and high operating temperature [9, 10].This has been a major hindrance in practical applications. Recently, there have been many attempts to improve its gas sensitivity and selectivity. *For this purpose, the studies have been carried out mainly following three directions: i) adding doped elements; ii)* combining with other SMOs; *iii) creating novel structure*. Among these research directions, doping can modify band structure to change optical and electrical properties of the material [11] e.g. Zn dopant can create the defect or traps in the band gap of SnO_2 to improve its optical properties [12]. Zn^{2+} has a radius (0.074 nm) close to that of Sn^{4+} (0.070nm) which is a favorable condition for Zn^{2+} to substitute for Sn^{2+} in the crystal lattice. The substitution elements break the bonds to create an acceptor energy levels or states near the valence band resulting in the increase in hole concentration by receiving electrons from valence band. This process is very useful to gas sensing applications [13]. Zn-doped SnO_2 has been indeed studied for humidity sensor [14], sulfur hexafluoride vapor sensor [15], formic acid gas sensor [16] and ammonia sensor [17]. In this study, pure SnO_2 and Zn-doped SnO_2 thin films are deposited on glass substrate by compressive sprayer deposition apparatus for alcohol vapor sensor.

2. CONTENT

2.1. Experimental

Deposition method: The thin films of SnO2 and Zn-doped SnO2 were deposited by a compress sprayer under the control of computer. The schematic diagram of the experimental setup published elsewhere [18] as showed in fig.1. The spray solution for pure SnO2 was prepared by dissolving SnCl2.2H2O into C2H5OH solvent. After 30 mins stirring, an appropriated amount of HCl was dropped slowly into the solution. The dropping process had finished when the pH of solution was appropriate 5 and solution became transparent.

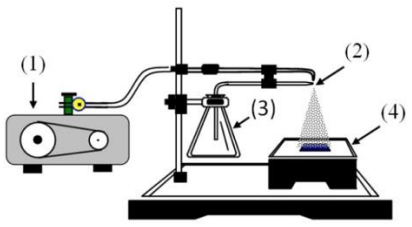

Figure 1. *Schematic diagram of experimental apparatus [18]*

(1)-Compressor, (2)-Spray nozzle, (3)-Solution tank, (4)-Heater

A predetermined amount of $Zn(CH_3COO)_2.2H_2O$ was added in to the solution to deposit the doped samples. After that, the solutions were sprayed on hot glass substrate with different temperature. Thanks to the chemical reactions, the films of pure SnO_2 and Zn-doped SnO_2 were formed on the substrate. Deposition temperature was carefully studied to find the optimum temperature to deposit the SnO_2 films. This temperature was then used to deposit Zn-doped SnO_2 thin films. Characterization methods: The crystal structures was studied by X-ray diffractometer (D8 ADVANCE BRUCKER) with Cu Kα radiation (λ = 0.154056nm). Surface morphology was observed by SEM (HitachiS-4800). The alcohol sensitivity was investigated by static method using a homemade system in which the resistance was measured by a Keithley 2000 multi-meter as showed in the figure 2.

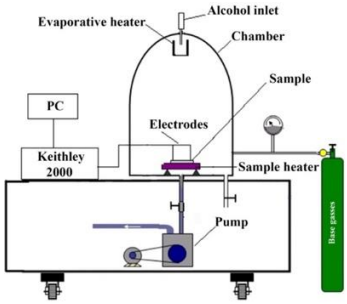

Figure 2. *Schematic diagram of gas sensor measurement system*

2.2. Result and discusión

The XRD results in fig.3 showed that no XRD peaks were found for the films deposited below 250°C. This indicated that the films were amorphous. Three XRD peaks corresponding to the tetragonal structural of SnO_2 (refer to JCPDS No. 77-0447) appeared for the films deposited at 370°C and the number of XRD peaks increased to eight with further increase in temperature. This indicated that the crystallization of the films was improved as the increase of deposition temperature. The films were crystalized well at temperature above 400°C. Therefore, the temperature of 400°C had been used for further experiments.

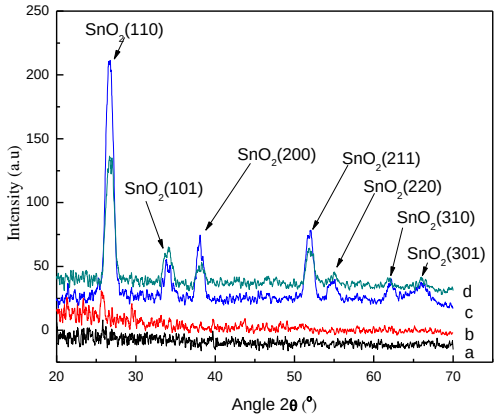

Figure 3*. XRD pattern of SnO_2 deposited on substrates at temperatures: a) 250°C; b) 370°C; c) 400°C d) 460°C.*

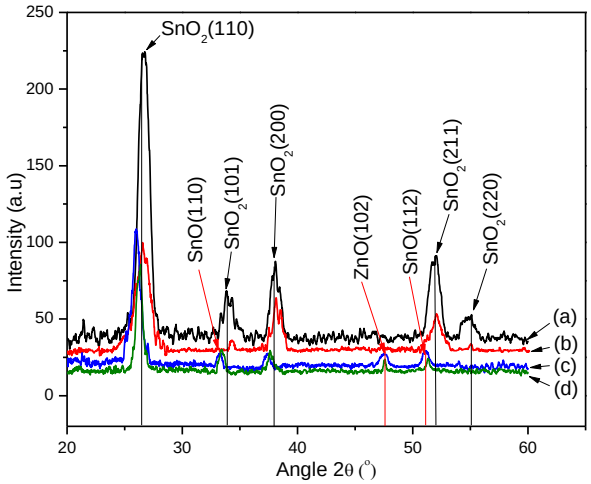

***Figure 4**. XRD pattern of Zn-doped SnO_2: a) 0%Zn; b) 2%Zn; c) 7% Zn; d) 10% Zn*

Figure 4 is Zn-doped SnO_2 films that deposited at 400°C with different Zn contents. The results showed that SnO_2 still retained the crystal structure when the Zn impurity content was up to 2%. Further increasing in Zn content, the films had more crystalline phases of zinc oxide. The diffraction peaks were shifted to the small angle when increasing the Zn content. The peak shift was believed to the substitution of Zn^{2+} for Sn^{4+} in the SnO_2 crystal lattice. Indeed, the ionic radius of Zn^{2+} (0.074 nm) is larger than that of Sn^{4+} (0.070 nm). The substitution should increase the distance between the lattice planes, resulting in shifting XRD peaks toward the small angle.

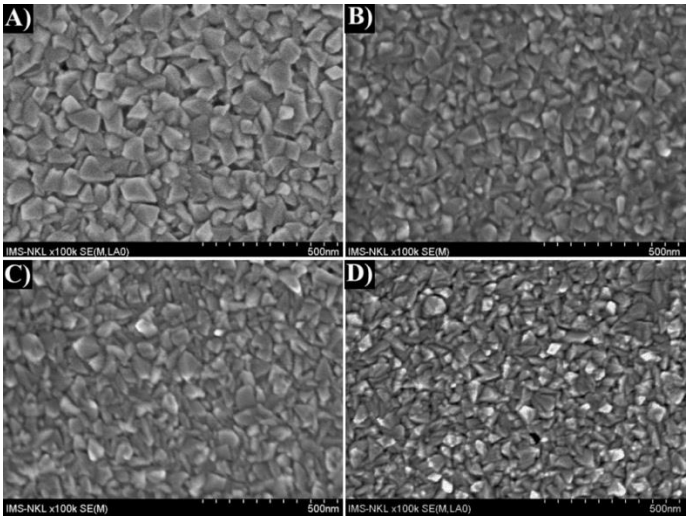

***Figure 5.** SEM images of Zn-doped SnO_2: A) 0% Zn; B) 2% Zn; C) 7%Zn; D) 10%Zn.*

SEM images of Zn-doped SnO_2 with different Zn content were showed on Fig. 5. The crystal size was less than 100 nm and decreased slightly as the increase of Zn doping content. The crystals were tetragonal crystalline shape that reconfirmed the crystal structure of SnO_2.

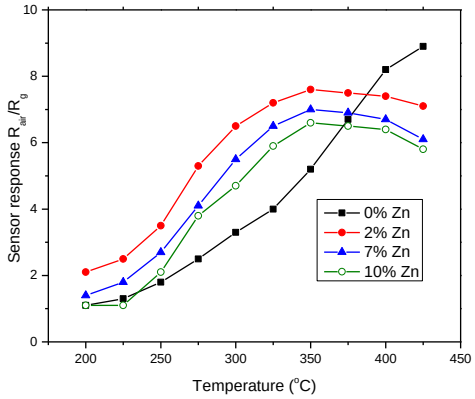

***Figure 6**. Influence of temperature on sensor response of pure SnO_2 and Zn-Doped SnO_2*

The influence of temperature on the alcohol gas sensivity of pure SnO_2 and Zn-doped SnO_2 films was investigated with the alcohol concentration of 0.4 mg/L (fig.6). For the pure films, their sensor responses have increased with temperature in the temperature range up to 425°C. The sensitivity of the film has not been studied at higher temperatures because it is no longer relevant for practical applications. For Zn-doped SnO_2 films, the sensor responses have increased with temperature up to 350°C. At higher temperature, the sensor responses decreased. There are two physico-chemical processes affecting sensitivity that occur simultaneously. The temperature promotes chemical reactions between the alcohol and the adsorbed oxygen that increase the sensitivity. On the other hand, temperature also promotes desorption of oxygen on the surface of the films that decrease the sensitivity. At high temperature, the desorption process dominates, so the sensitivity tends to decrease. This is the reason why the optimum operation temperature of the films for detecting alcohol is 350°C.

Zn impurity in SnO_2 crystals influence strongly on the sensitivity of doped films as described in fig.6. The substitution of Zn^{2+} for Sn^{4+} provides more oxygen vacancies for SnO_2, resulting in more oxygen species adsorbed on the surface of SnO_2 and more surface oxygen vacancies in the Zn-doped SnO_2. Therefore, the Zn-doped SnO_2 sensor shows a higher response [19]. XRD pattern in fig.4 showed that the Zn impurity content of 2% exhibited the optimum substitution of Zn^{2+} for Sn^{4+}. This is the reason why the films doped with 2% Zn showed the best sensor response.

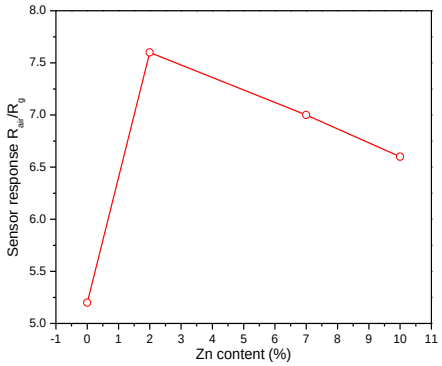

***Figure 6**. Influence of Zn impurity content on the sensor response of the films at 350°C*

The influence of alcohol vapor on the sensivity of 2% Zn- doped SnO_2 was studied at temperature of 350^{o}C. The sensor response increases with the increase in alcohol vapor concentration up to 1.2 mg/L. Further increase in the concentration, the sensor response tends to approach to saturation value. The reaction between alcohol vapor and adsorbed oxygen causes the change of the sensor response. At low vapor concentrations, the chemical reactions are weak, so the sensor response is low. Increasing the vapor concentration should promote chemical reactions, causing an increase in sensor response. However, if the vapor concentration is increased to a value at which all of adsorbed oxygen reacts completely with the alcohol vapor, the response will be saturated.

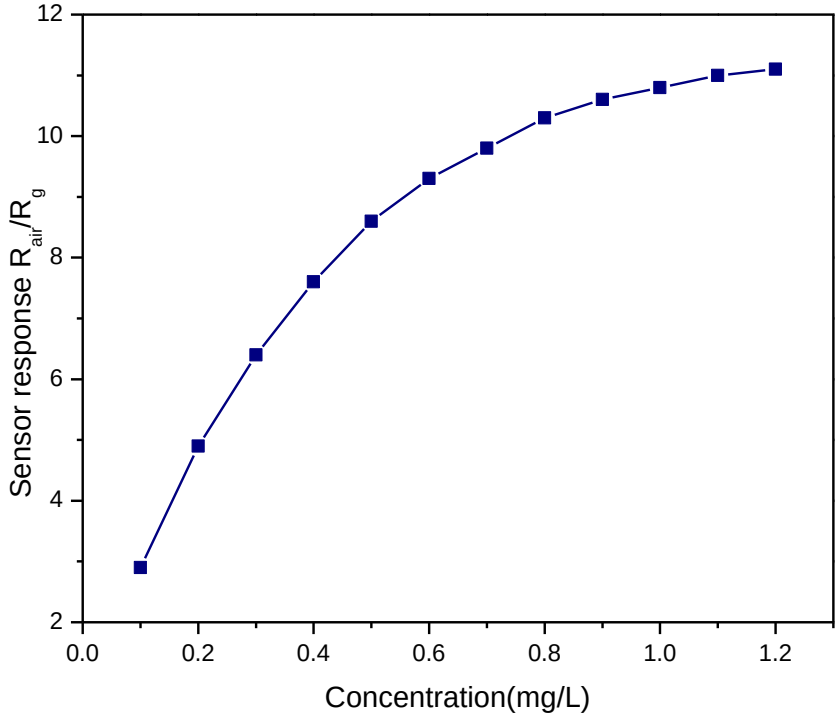

Figure 7. *Influence of alcohol vapor on the sensivity of 2% Zn- doped SnO_2*

3. CONCLUSION

The Zn-doped SnO_2 crystals were successfully deposited on hot substrate by compressed spray method. The films were crystalized well at 400^{o}C with body centered tetragonal structure. The crystals have tetragonal shape with the size was less than 100 nm and decreased slightly as the increase of Zn doping content. Zn-doped with 2% exhibited an optimum content due to the fine structure and the best sensitivity. The operation temperature and the saturation alcohol vapor concentration that gave the best film sensitivity is 350^{o}C and 1.2 mg/L, respectively.

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CHẾ TẠO MÀNG MỎNG SnO_2 PHA TẠP Zn BẰNG PHƯƠNG PHÁP PHUN ÁP SUẤT ỨNG DỤNG CHO CẢM BIẾN NHẠY HƠI CỒN

***Tóm tắt**: Màng mỏng SnO_2 và SnO_2 pha tạp Zn được phủ trên đế thủy tinh bằng hệ phun áp suất sử dụng muối $SnCl_2.2H_2O$ và Zn $(CH_3COO)_2.2H_2O$ làm tiền chất. Ảnh hưởng của nhiệt độ chế tạo và nồng độ tạp chất Zn lên cấu trúc tinh thể của màng SnO_2 và SnO_2 pha tạp Zn đã được khảo sát bằng XRD. Kết quả cho thấy màng SnO_2 với cấu trúc tứ giác đã bắt đầu kết tinh ở nhiệt độ 370°C và kết tinh tốt ở nhiệt độ trên 400°C. SnO_2 vẫn giữ nguyên cấu trúc tinh thể khi nồng độ tạp chất Zn lên đến 2%. Nếu tiếp tục tăng nồng độ Zn tăng hơn nữa thì sẽ có thêm nhiều pha tinh thể của oxit kẽm. Hình thái bề mặt của các màng quan sát bằng ảnh SEM cho thấy các tinh thể SnO_2 phân bố khá đồng đều với kích thước nhỏ hơn 100nm. Kích thước tinh thể giảm nhẹ khi nồng độ tạp chất tăng. Tạp chất ảnh hưởng rất nhiều đến độ nhạy hơi cồn của màng. Độ nhạy của màng tinh khiết tăng lên khi nhiệt độ làm việc của nó tăng lên. Tính chất này vẫn còn duy trì ngay khi ở vùng nhiệt độ khá cao. Độ nhạy của màng pha tạp Zn tăng lên khi nhiệt độ làm việc của nó tăng lên đến 350oC. Nhiệt độ tăng hơn nữa sẽ làm giảm độ nhạy. Ở nhiệt độ làm việc tối ưu, các màng pha tạp với nồng độ 2% Zn thể hiện độ nhạy tốt nhất.*

***Từ khóa**: SnO_2, SnO_2 pha tạp Zn, độ nhạy hơi cồn, hệ phun áp suất.*