HNUE JOURNAL OF SCIENCE
Natural Sciences 2024, Volume 69, Issue 3, pp. 26-34
This paper is available online at http://hnuejs.edu.vn/ns
DOI: 10.18173/2354-1059.2024-0032

THE PREPARATION OF Al-DOPED ZnO THIN FILMS BY SPRAY PYROLYSIS TECHNIQUE FOR ALCOHOL VAPOR SENSOR

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Received July 25, 2024. Revised August 22, 2024. Accepted October 30, 2024.

Abstract. Thin films of ZnO and Al-doped ZnO are deposited on glass wafer substrates using a compressed sprayer system with $Zn(CH_3COO)_2.2H_2O$ and $AlCl_3$ as precursors. The influence of Al doping concentration on the crystal phase and morphology of the samples is investigated by XRD and SEM, respectively. The results show that the films have been crystallized in the form of the wurtzite hexagonal phase of the ZnO lattice, and the addition of Al does not change the ZnO crystal structure. Despite this, SEM images show that added Al significantly affects the particle size of the samples. The particle size decreases and becomes more uniform as the Al concentration increases up to 7%. Further increasing the Al concentration causes the particles to agglomerate into clusters. The resistance measurements show that the sheet resistance of the films decreases in the presence of the Al dopant, providing evidence that Al has been successfully doped into the ZnO crystal lattice. An appropriate amount of Al dopant can improve the alcohol vapor sensitivity of the film. The ZnO film doped with 7% Al exhibits the best alcohol sensitivity.

Keywords: Al-doped ZnO, alcohol vapor sensor, spray pyrolysis.

1. Introduction

Alcohol vapor sensors play a crucial role in various fields due to their ability to detect and measure the concentration of alcohol in the air. These sensors are pivotal in ensuring safety, particularly in industries where the presence of alcohol vapors can pose significant risks. For instance, in the automotive industry, alcohol vapor sensors are essential components of breathalyzer devices, which law enforcement agencies use to measure blood alcohol content in drivers [1]-[4]. This application helps prevent drunk driving, thereby reducing road accidents and enhancing public safety. In the workplace, especially in environments where the handling of alcohol and other volatile organic compounds is common, these sensors are vital for maintaining a safe working environment. They provide early warnings of high alcohol vapor levels, allowing for timely interventions to prevent potential hazards such as fires or explosions. This is particularly important in chemical plants, breweries, and laboratories.

Alcohol sensors based on zinc oxide (ZnO) materials have garnered significant attention due to their high sensitivity, selectivity, and stability [5]-[7]. ZnO is a semiconductor material known for its excellent electronic properties and high surface-to-volume ratio, making it an ideal candidate for detecting volatile organic compounds such as ethanol. The unique properties of ZnO enable it to interact effectively with ethanol molecules, resulting in measurable changes in electrical resistance that can be accurately detected and quantified. These properties are further enhanced by doping ZnO with other elements, which can tailor its sensing properties to specific needs [8]-[11]. Innovations such as nanostructured ZnO and hybrid materials are expected to further enhance their sensitivity and selectivity, paving the way for even broader applications [12]-[14]. Al-doped ZnO sensors introduce additional benefits through the incorporation of aluminum atoms into the ZnO lattice. This doping process enhances the conductivity and electron mobility of the ZnO material [15], leading to improved sensor response times and greater sensitivity to ethanol at lower concentrations [16]-[18]. The presence of aluminum also modifies the surface properties of ZnO, increasing its selectivity towards ethanol while reducing the influence of other gases and potential contaminants [19]. This heightened selectivity makes Al-doped ZnO sensors especially suitable for environments with mixed gases, such as industrial settings and environmental monitoring.

Recently, several studies have addressed the alcohol vapor sensitivity of Al-doped ZnO films. However, these studies have not been truly comprehensive. Most studies have focused on Al impurity concentrations below 5% [17], [18]-[25] and have investigated only one alcohol concentration [6], [25] or used a very high alcohol concentration range (greater than 1000 ppm) [18]. If Al substitutes for Zn, the electrical conductivity of the film should increase. Unfortunately, there have been no studies on the effect of Al impurities on the sheet resistance [5], [17], [18], [25], which means the evidence for Al being successfully doped into the ZnO crystal lattice is not fully convincing. This study investigates the effect of Al impurity concentrations up to 10% on the alcohol sensitivity and sheet resistance of the films to develop alcohol vapor sensors.

2. Content

2.1. Experiment

**** Deposition method:*** The thin films of ZnO and Al-doped ZnO are deposited using a compressed sprayer under computer control. The schematic diagram of the experimental setup was published elsewhere [20]. The spray solution for pure ZnO is prepared by dissolving $Zn(CH_3COO)_2.2H_2O$ in C_2H_5OH at a molarity of 0.2M. After 60 minutes of stirring, an appropriate amount of HCl is dropped slowly into the solution. The dropping process finished when the pH of the solution was appropriate at 5 and the solution became transparent. The dopant solutions are prepared by adding an appropriate amount of $AlCl_3$ to the pure solution. The concentration of Al dopant is calculated based on the amount of Al in the $Zn(CH_3COO)_2 \cdot 2H_2O$ and $AlCl_3$ mixture. The solution is then sprayed onto a hot glass substrate at 400 ^oC. Due to the thermal decomposition reaction, ZnO and Al-doped ZnO films are formed.

*** Characterization methods:** The crystal structures are studied using an X-ray diffractometer (D8 ADVANCE BRUCKER) with Cu Kα radiation (λ = 0.154056 nm). Surface morphology is observed by SEM (HitachiS-4800). The alcohol sensitivity is investigated by the static method using a homemade system as shown in Fig. 1. Standard alcohol vapor with a concentration of 3830 ppm is created by evaporating 100 µl of alcohol in a 10 l vapor chamber (chamber 1). The sample and sample heater are placed in a measuring chamber (chamber 2). The sample electrodes are connected to a Keithley 2000 multimeter interfaced with a computer to observe resistance changes.

The resistance measurement over time starts with clean air while the two valves of chamber 2 are closed. Next, an amount of alcohol vapor taken from chamber 1 is pumped into the inlet of chamber 2. The concentration of alcohol vapor is determined by the ratio of the volume of alcohol vapor introduced into chamber 2 to the volume of chamber 2. After the resistance of the sample drops to a stable value, both valves are opened, and the pump is used to extract the alcohol-containing gas at the outlet while allowing clean air to flow into the inlet. The resistance of the sample quickly returns to its original state. The process is repeated with different alcohol vapor concentrations until the measurement is completed. The sensor response which is determined as the R_a/R_g ratio (where R_a and R_g are the resistances of the sensor in the ambiance air and air-gas mixture respectively), is recorded in the computer as a text file.

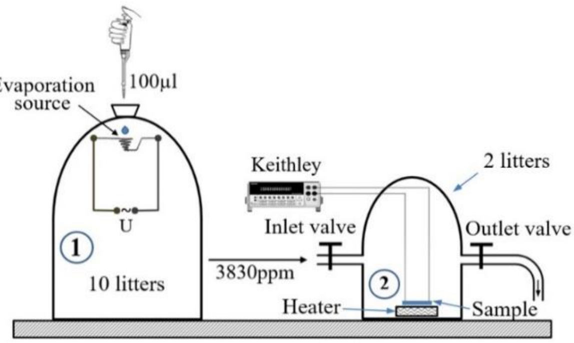

Figure 1. Schematic diagram of gas sensor measurement system

2.2. Result and discussion

Figure 2 shows the X-ray diffraction patterns of Al-doped ZnO films deposited with different Al concentrations at 400°C. Sharp diffraction peaks at 2θ angle positions of 31.81°, 34.46°, 36.29° and 47.58° corresponding to the diffraction planes (100), (002), (101), and (102) of the Wurtzite hexagonal phase of ZnO lattice (JCPDS data card No. 36-1451) have been observed. This proves that ZnO has been well crystallized. No other phases related to Al or other aluminum compounds were found, indicating that the addition of Al does not change the ZnO crystal structure. Additionally, the intensity of the diffraction peaks tends to decrease with increasing Al concentration. The reduction in crystallinity of the Al-doped films may be due to aluminum facilitating the creation of more nucleation sites, thereby inhibiting the crystallization process [17]. Studies on Al-doped ZnO films have shown that when Al substitutes for Zn in the ZnO crystal lattice, the intensity of the diffraction peaks decreases with increasing Al dopant concentration [21]-[27].

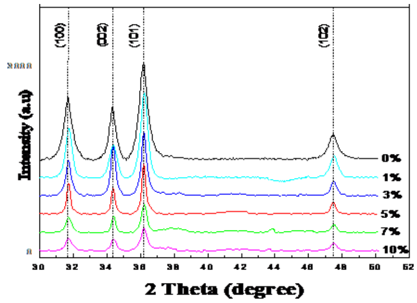

***Figure 2*. XRD pattern of Al-doped ZnO deposited on substrates with different Al concentration**

Figure 3 shows the change in the sheet resistance of Al-doped ZnO thin films with different Al dopant concentrations measured at room temperature. The sheet resistance of the samples tends to decrease with increasing dopant concentration up to 7%. Further increasing the amount of Al causes the sheet resistance to increase. When an Al atom (valence III) substitutes for a Zn atom (valence II) in the ZnO crystal lattice, an additional free electron is created. This is the reason for the decrease in sheet resistance of Al-doped ZnO films. However, the conduction mechanism of semiconductor thin films is quite complex. Besides conduction due to the charge carriers in the semiconductor, phenomena occurring at the grain boundaries also play a very important role. Oxygen adsorbed on grain boundaries causes a potential barrier that prevents the movement of charged particles, reducing conductivity (i.e., increasing resistance). Therefore, the sheet resistance of the semiconductor is always unstable in the presence of air. This is why the sheet resistance curve is not smooth. This is an inherent property of semiconductor thin films that is very difficult to control. This is not too serious because small changes in air resistance do not significantly affect the sensor response results. A large amount of added Al may create unwanted elements at the grain boundaries because not all Al atoms substitute for Zn. This will increase the resistance of the film. Despite that, the trend of decreasing sheet resistance in the thin films is considered indirect evidence that Al has been successfully doped.

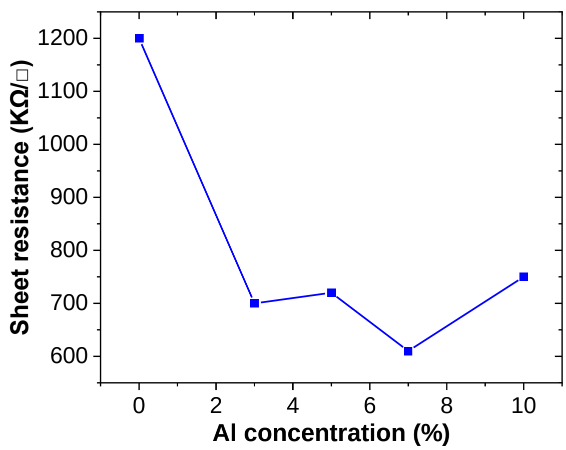

***Figure 3*. The sheet resistance of the films versus Al dopant concentration at room temperature**

Figure 4 shows the SEM images of Al-doped ZnO with different Al concentrations and the particle size distribution. The particle size tends to decrease and become more uniform as the Al doping concentration increases. However, when the doping concentration reaches 10%, the particles aggregate into clusters with a size of about 300 nm. The particle size distribution calculated from SEM images using ImageJ software shows that the distribution peaks of the undoped sample are relatively broad, indicating that the particles are not uniform. Particles with a size of about 120 nm occupy most of the sample surface area. The distribution peaks gradually narrow when the Al dopant concentration is increased up to 7%, indicating that added Al makes the particles more uniform. However, further increasing the amount of Al dopant causes the distribution peaks to broaden again. The 7% doped sample exhibited the highest uniformity, with the majority of particles having sizes between 50 nm and 60 nm.

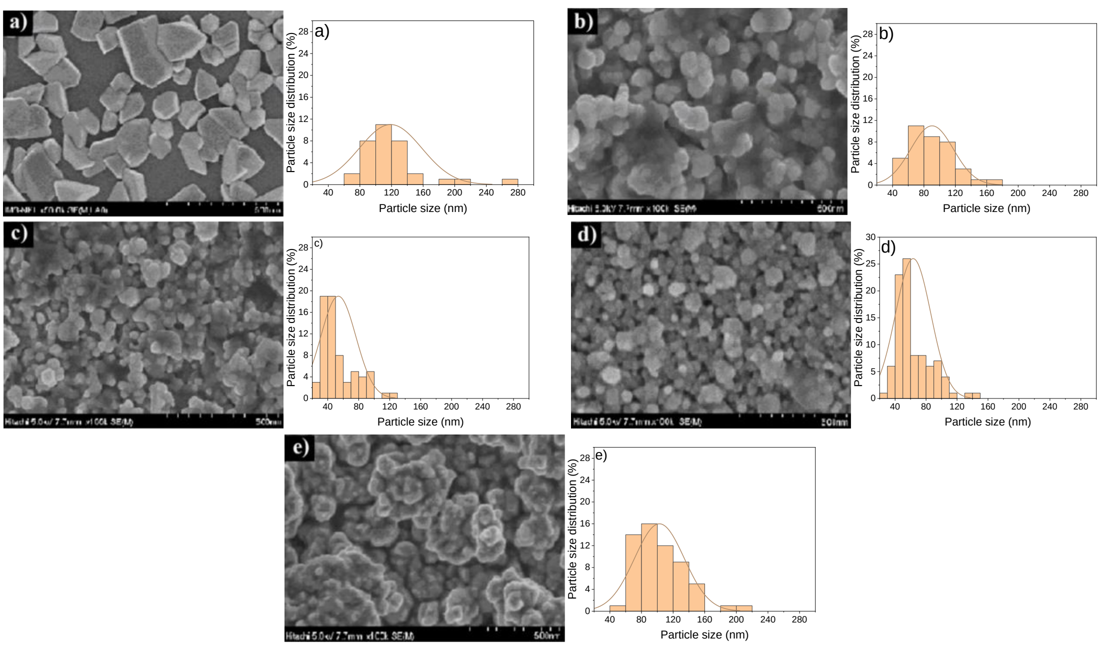

Figure 4. SEM images of Al-doped ZnO: a) 0 % Al; b) 3% Al; c) 5%Al; d) 7%Al; e) 10%Al

Gas sensors typically operate at high temperatures, so the effect of operating temperature on gas sensitivity is usually investigated before studying other properties of the sensor. In this study, the effect of temperature on the alcohol vapor sensitivity of Al-doped ZnO thin films was investigated with an alcohol vapor concentration of 3000 ppm (Figure 5). The results show that all doped and undoped samples exhibit almost no response to alcohol vapor at 150 °C. The sensor response increases sharply when the operating temperature rises above 200 °C. At temperatures exceeding 250 °C, the sensor response begins to increase slowly and tends to reach a saturation point. These results are consistent with those reported in previous studies [6], [17], [18]. For sensor applications, higher operating temperature ranges become less meaningful. Therefore, the temperature of 250 °C was chosen for further studies.

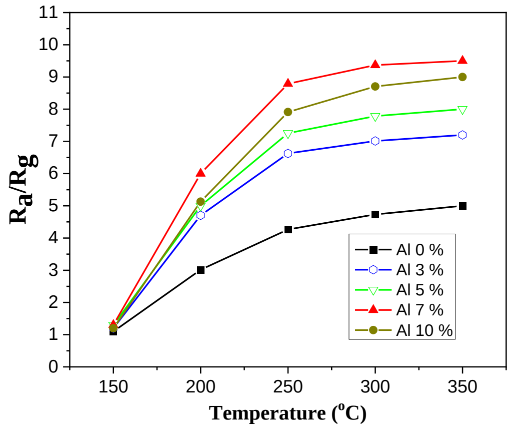

Figure 5. Influence of temperature on the sensor response of pure ZnO and Al-Doped ZnO

The effect of Al dopant concentration on the sensitivity of the sensor based on Al-doped ZnO films has been studied at a temperature of 250 °C (Figure 6). The response and recovery time of the sensor to alcohol vapor in Figure 6(a) shows that the sensor responds very quickly to changes in alcohol vapor concentration. The effect of Al dopant concentration on the sensor response to different alcohol vapor concentrations is shown in Figure 6(b). The results show that the Al dopant concentration significantly affects the sensor response. At the same alcohol vapor concentration, the sensor response increases as the Al dopant concentration increases up to 7%. Further increasing the Al dopant concentration results in a decrease in the sensor response.

ZnO is an n-type semiconductor with electrons as free charge carriers. When exposed to air, ZnO will adsorb oxygen in the form of O^{2-}, O^- and remove its conduction electrons, causing the resistance of the sample to increase. The adsorption process is described by the following reactions [18]:

$$O_{2(gas)} \leftrightarrow O_{2(adsorbed)}$$

$$O_{2(adsorbed)} + e^- \leftrightarrow O_{2(ads)}^-$$

$$O_{2(ads)}^{2-} + e^- \leftrightarrow 2O(lat)^{2-}$$

where the subscripts gas, ads, and lat mean gas, adsorbed, and lattice, respectively.

In the presence of alcohol vapor, the adsorbed oxygen reacts with the alcohol vapor, releasing electrons back into the sample and causing the resistance of the samples to decrease rapidly. This process is described by the following reaction:

$$CH_3CH_2OH_{ads} + 6O_{ads}^- \rightarrow 2CO2 + 3H_2O + 6e^-$$

Doped samples have more free electrons, so they can adsorb more oxygen. Therefore, when doped with Al, the Al-doped ZnO film has a higher response to alcohol vapor. Additionally, grain size plays a vital role in improving the sensitivity of the films. Electron transfer processes mainly occur at grain boundaries, so smaller grain sizes have a stronger effect (since the total grain boundary area per unit mass is larger). The SEM image in Figure 4(e) shows that if too much Al is doped, the grains become agglomerated, leading to a decrease in the total surface area of the grain boundaries. This is the cause of the reduced sensitivity of the films, as shown in Figure 6.

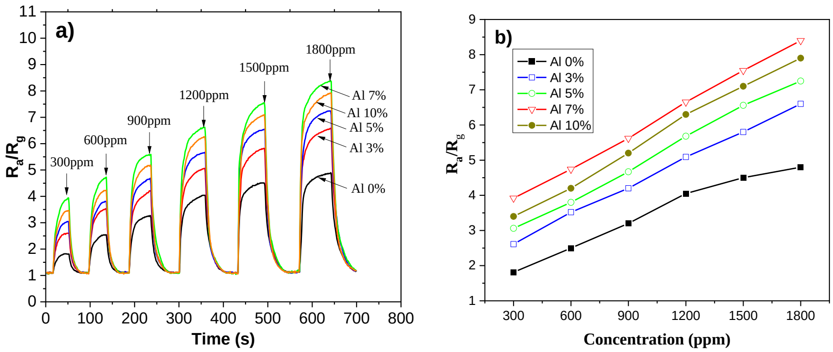

Figure 6**. **Influence of Al impurity concentration on the sensor response of the films at an operating temperature of 250°C: a) response and recovery time; b) sensor response **versus** ***alcohol vapor***

3. Conclusions

Al-doped ZnO crystals with a single wurtzite hexagonal structure were successfully deposited on a hot substrate at 400 °C using the compressed spray method. The concentration of the Al dopant does not change the crystal lattice structure of the ZnO thin films, but it significantly affects their particle sizes. The particle size becomes smaller and more uniform when the Al dopant concentration is below 7%. At higher Al concentrations, the particles tend to agglomerate. Al-doped thin films exhibit good sensitivity to alcohol vapor. The Al-doped sample with a concentration of 7% has the highest sensitivity to alcohol vapor. This indicates the potential application of Al-doped ZnO films as alcohol vapor sensors in devices measuring alcohol vapor concentration.

Acknowledgment. This work is supported by the VNU University of Engineering and Technology under project number CN22.02.

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