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# Characterization of Doped ZnO Thin Film for Ammonia Gas Sensing Application

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This paper reports on the characterization of Sn- and Al-doped zinc oxide thin film for potential ammonia gas detection. The sol–gel method has been used to deposit the dopant onto the glass substrate at an annealing temperature of 500°C for three different doping concentrations, which are 0.5, 1.0, and 1.5 at.%. The method used to produce this thin film is sol–gel, as it is cheap, easy, and can be employed at low temperatures. The studies involve the investigation of the morphological structures and electrical and optical properties of doped ZnO. In terms of structural properties, scanning electron microscope images of Sn- and Al-doped ZnO change as the dopant concentration is increased. The doped thin film response and recovery towards 200 ppm of ammonia were observed and recorded. Both dopants show good gas sensing response. The recorded resistance reading suggests that Al is the superior dopant in gas sensing as it produces a low resistance reading of 230 Ω as opposed to 140 kΩ produced by Sn-doped ZnO thin film.

topics: gas sensor, semiconductor, ammonia, doped ZnO thin films

## 1. Introduction

Ammonia ($NH_3$) is a colorless, smelly nitrogen and hydrogen gas found in agriculture, household, and commercial cleaning products [1]. Ammonia is an irritant and corrosive substance. The nose, throat, and respiratory system will be swiftly burnt if exposed to high levels of ammonia in the air. Low amounts of ammonia in the air or solution might cause immediate skin or eye discomfort [2].

Metal oxide semiconducting (MOS) gas sensors are inexpensive and have a high level of vapor detection accuracy. They are good candidates for commercial gas detectors because of their simplicity of manufacture, high ruggedness, and simple interface electronics. Zinc oxide (ZnO) was chosen as one of the favorite metal oxide semiconductor elements because it has a large band gap of 3.37 eV, which allows it to be modified by adding dopants to boost electron mobility and lower the band gap of thin films [3]. ZnO gas sensors typically operate at high temperatures ranging from 300 to 500°C. To address this issue, ZnO gas sensor preparation techniques and doping can assist in lowering operating temperature while also enhancing material stability, sensitivity, and selectivity. The electronic characteristics of ZnO solids may be tweaked using a variety of dopants, most commonly group 13 elements, including aluminum (Al), tin (Sn), gallium (Ga), and indium (In).

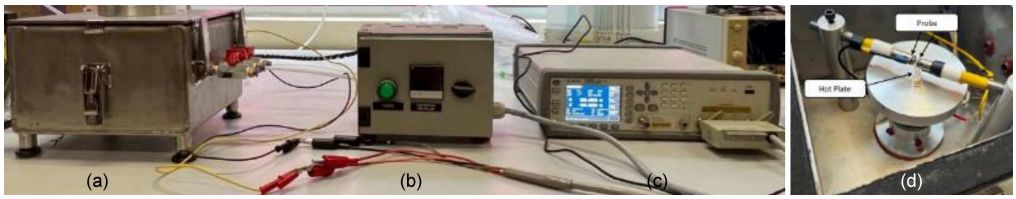


Fig. 1. Ammonia measurement setup with (a) closed chamber, (b) temperature controller, (c) LCR meter, and (d) inside view of closed chamber, where the sensor is placed on the hot plate, and the probe to connect it to LCR meter for resistance recording.

Some of the technologies that have been introduced for ZnO gas sensor preparation include sputtering, thermal evaporation, radio frequency (RF) sputtering using a magnetron, reactive sputtering with a direct current magnetron, co-electrodeposition, the sol–gel technique, and thermal decomposition. The sol–gel process provides the most flexibility in terms of creating vast areas of zinc oxide (ZnO) coating for technological applications [4]. One of the elements that has been doped with ZnO is tin (Sn). Tin is one of the elements that can help improve the structural and electrical characteristics of ZnO. This combination is appropriate for a chemical sensor. Sn has a high heat conductivity, which affects thin film resistance.

Doping ZnO with other elements is one technique to improve gas sensing characteristics. Dopants affect the structure and surface area of thin film crystals based on loading concentration and inherent features like atomic size and charge. Finding the right dopant to dramatically improve ZnO ammonia gas detecting capability is difficult since each dopant has its own set of features, and uniform dispersion of the solution is difficult [5]. The sol–gel method is both cost-effective and simple to use. It is also quite homogeneous and can be worked with at low temperatures. It also ensures a strong bond between the substrate and the topcoat material. Hence, in this paper, the sol–gel method will be used to prepare ZnO solutions doped with two dopants, namely Sn and Al. The effect of dopants on ZnO will be characterized in terms of morphology, and the doped thin film will be exposed to ammonia gas, and its sensing response will be recorded.

## 2. Materials and method

Doped ZnO solutions were prepared using the sol–gel method following our previous work [6]. The concentrations of both Sn and Al dopants were set to 0.5 at.%, 1.0 at.%, and 1.5 at.%. The resultant solution was stirred at 80°C for 1 h. Then, the solution was aged for 24 h to yield a homogenous solution. Spin coating was used to prepare the ZnO and dopant solution at the rotation speed of 2000 rpm for 60 s. Then, the thin film was soft-baked for 10 min at 150°C. The process of spin coating and soft baking was repeated 6 times. After that, the samples were annealed in a furnace at 500°C for 5 h. A scanning electron microscope (SEM) was used to investigate the morphological structures of the film. The prepared solution was then spin-coated on Au interdigitated electrode at 500 rpm for 40 s. Then, the electrode substrate was soft-baked for 10 min at 150°C to remove any organic residue. The ammonia measurement physical setup is shown in Fig. 1.

The electrode is placed inside the closed test chamber ($25 \times 15 \times 25$ cm$^3$) on a hotplate. The test chamber is connected to a temperature controller that sets the chamber to a certain temperature so that the device can operate as a gas sensor. The variation in resistance values is recorded using the E4980A Precision LCR Meter.

## 3. Results and discussion

In SEM images in Fig. 2, it can be observed that there is a significant difference in terms of the structure of the grains between the undoped and doped thin films. This obviously shows the strong dependence of the surface structure on the tin doping concentration [7]. Undoped ZnO appears to be closely packed with non-spherical particles of a hexagonal wurtzite structure and evenly spread on the film surface.

However, Sn-doped ZnO has completely different crystal structures, with their own sizes and shapes of crystals, for dopant concentration changing from 0.5 at.% to 1.5 at.%. It seems that the material is not as tightly spread as in the case of the undoped structure. There is a variant shape that appeared at both 0.5 and 1.0 at.% concentrations. Sn is detected due to its tetragonal-shaped crystal structure, as shown in Fig. 2b–d.

The shape is confirmed to be Sn because Ilican et al. [8] found that Sn has a tetragonal crystalline structure, as shown in Fig. 2. There is also visible white shining in certain parts for undoped ZnO and with 0.5, 1.0, and 1.5 at.% Sn dopant concentration. According to [7], this phenomenon is known as a white cluster, which is caused by electrons assembled at the film surface. Here, instead, it is due to the uneven surface of the ZnO films deposited on the glass substrate. The SEM images of Al-doped ZnO also change as the dopant concentration is increased (see Fig. 2e and f). Al dopant with

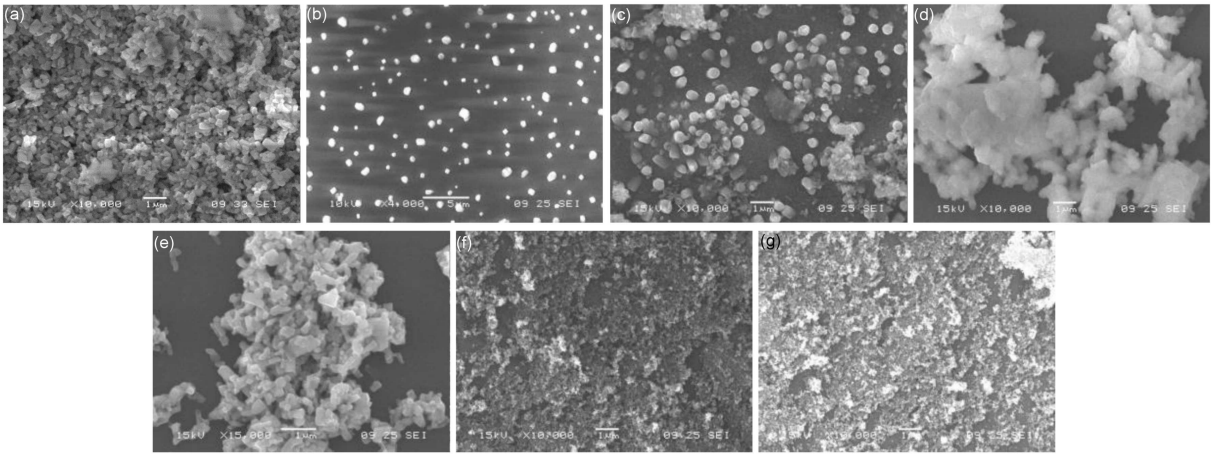


Fig. 2. SEM images of (a) undoped ZnO and ZnO doped with Sn dopant concentration of (b) 0.5 at.%, (c) 1.0 at.%, (d) 1.5 at.%, and Al dopant concentration of (e) 0.5 at.%, (f) 1.0 at.%, (g) 1.5 at.%.

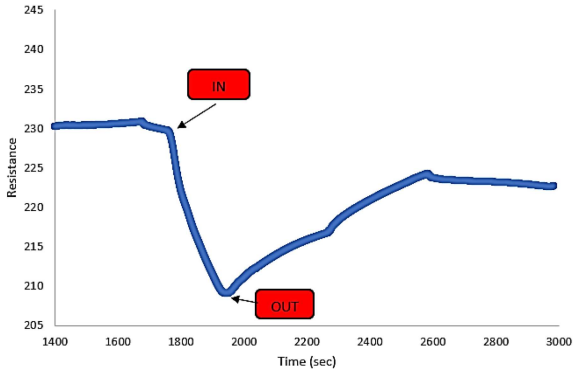


Fig. 3. Response and recovery of Al-doped ZnO at the exposure of 200 ppm ammonia.

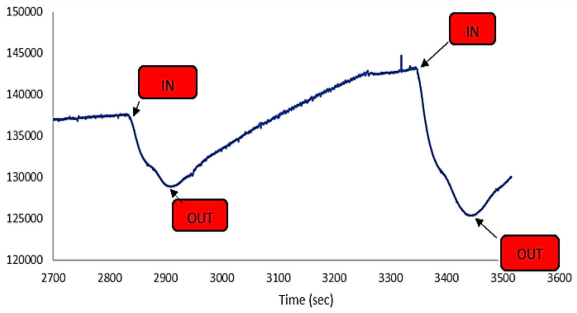


Fig. 4. Response and recovery of Sn-doped ZnO at the exposure of 200 ppm ammonia.

the lowest concentration seems not to be evenly distributed at some areas of the surface. However, it can be observed that the dopants are wrapped around the ZnO particle, as shown in Fig. 2e.

An Agilent LCR meter was used to measure the electrical characteristics of doped ZnO thin films. The DC two-probe method was used to measure the resistivity of the doped ZnO films exposed to ammonia. For initial proof of application, only doped ZnO with 0.5 at.% dopant concentration was used for ammonia gas sensing. For gas sensing applications, there are a few sensing performances that are typically analyzed, such as sensitivity, stability, response time, and recovery time [9]. However, in this work, we only focus on the response and recovery of the sensor as we want to prove the main concept of metal oxide semiconductor gas sensing. The experiment was conducted using both Sn- and Al-doped thin films. Response and recovery time is the time required for a sensor to achieve and return to 90% of the original baseline signal upon injection and removal of targeted gas. Figure 3 shows the ammonia detection response and recovery for Al-doped ZnO at the temperature of 120°C.

Based on the presented figures, it can be seen that the doped thin film reacts to ammonia exposure at a concentration of 200 ppm. Initially, dry air flowed into the chamber for 10 min. This was to ensure that the chamber was not contaminated with outside particles that could affect the ammonia sensing. After that, the flow of dry air was turned off, and ammonia flowed into the chamber for 10 min. For Al-doped ZnO, the resistance dropped from 230 to 210° when ammonia was introduced after 200 s. After 5 min, the ammonia was turned off and we could see that the resistance increased gradually to its original resistance value. This shows that the sensor responds well to the ammonia exposure in the chamber.

For the Sn-doped ZnO (Figure 4), the initial resistance value once ammonia is introduced is recorded at 137 kΩ, and it drops to 127 kΩ after approximately 200 s after ammonia introduction. When the gas was turned off, the resistance value returned to a slightly higher resistance of 142 kΩ, 3.5% higher than the initial resistance value. The gas flow was turned on again after 10 min, and the resistance showed a similar reading pattern as the first gas cycle of gas exposure. This shows that Sn-doped ZnO has good a response towards ammonia gas.

Metal oxide semiconductor gas sensing mechanism depends on the structural response and change in resistance due to the adsorption and desorption of the target gas molecules.

In terms of dopants, the resistance reading suggests that Al is the superior dopant in gas sensing as it produces a low resistance reading of 230 Ω as opposed to 140 kΩ produced by Sn-doped ZnO thin film. This implies that the Al atoms are successfully incorporated in the ZnO lattice as Al dopants provide higher conductivity due to the small ionic radii of Al atoms. ZnO is a metal oxide semiconductor with a wide band gap of 3.37 eV and a large binding energy of 60 meV [10]. This wide band gap has a lot of advantages since it can withstand high temperatures, has mechanical robustness, and is stable [11]. The gas sensing mechanism is based on the chemiresistivity principle, where when atoms or molecules interact with the surface of a metal oxide semiconductor, it affects the conductivity of the sensor. ZnO detects gas through the changes in resistance of the material because resistance changes when exposed to the targeted gas [12]. In general, there are two functions in chemical sensors, i.e., a receptor function and a transducer function. The function of the receptor is to recognize the chemical substance, while the transducer transduces the chemical substance into an output signal. When a metal oxide semiconductor interacts with the target gas, it will act as the donor or acceptor of charge carrier, which is called the receptor function, and then will change the resistivity of the metal oxide semiconductor (transducer function). The value of the resistance depends on the majority carrier in the metal oxide semiconductor and the targeted gas. When Sn and Al dopants are introduced, it will change the surface morphology and grain size of the ZnO thin film. The grain size of doped ZnO reduces as the dopant prevents the crystal structure growth rate. This will improve the sensing performance as a small-sized particle has a high surface area, consequently improving the chemisorbed oxygen ions. The initial results of gas sensing performance reported in this paper suggest good agreement with the previously reported work [13], as similar patterns in gas response and recovery have been obtained.

## 4. Conclusions

Sn- and Al-doped ZnO thin films were successfully deposited using the sol–gel method for three different concentrations of 0.5, 1.0, and 1.5 at.%. Surface morphology characterization was conducted using SEM. For undoped ZnO, hexagonal wurtzite structures are visible, and dopants have been observed to be wrapped around the ZnO structure. As the dopant concentration increased, the structures became slightly bigger and less smooth. Resistance measurements indicate that Al is a better dopant for gas sensing than Sn because it provides low resistance readings of 230 Ω as opposed to 140 kΩ for ZnO thin films that are doped with Sn.

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