Enhanced Acetone Sensing Using Ag-doped ZnO Thin Films for Breast Cancer VOC

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Abstract— Acetone sensing is crucial in various applications, including environmental monitoring, breath analysis for medical diagnostics, and industrial safety. Zinc oxide (ZnO) is a widely used metal oxide semiconductor for gas sensors due to its high sensitivity, chemical stability, and ease of synthesis. However, the pristine ZnO-based sensors often suffer from high operating temperatures and limited selectivity. In this work, silver (Ag) doping is introduced to enhance the acetone-sensing properties of ZnO, focusing on improving sensitivity, selectivity, and reducing operating temperatures.

Ag-doped ZnO nanostructures were synthesized using a facile chemical route and characterized using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The doping of Ag into the ZnO lattice creates oxygen vacancies and enhances the catalytic activity, facilitating improved acetone adsorption and reaction kinetics on the sensor surface. Gas-sensing tests revealed that Ag-doped ZnO exhibits significantly enhanced sensitivity to acetone at lower temperatures compared to undoped ZnO. The sensor's response to various concentrations of acetone was in-vestigated, demonstrating superior selectivity against interfering gases like ethanol and methanol.

The findings suggest that Ag-doped ZnO is a promising material for low-temperature, high-performance acetone gas sensors, offering potential for applications in non-invasive disease diagnostics, particularly for detecting diabetes through breath acetone analysis.

Keywords: Acetone sensing, Ag-doped ZnO, sol-gel method, breast cancer VOC detection, MSM structure, surface character-ization, I-V characterization.

I. INTRODUCTION

Breast cancer is a major global health concern, accounting for a significant proportion of cancer diagnoses in women [1]. Early detection is crucial to improving treatment outcomes and survival rates. Traditional diagnostic methods, such as mammography and biopsy, are often invasive or costly, which has spurred interest in non-invasive diagnostic techniques like breath analysis for detecting disease-specific volatile organic compounds (VOCs).

Acetone is one of the VOCs identified in exhaled breath that shows promise as a biomarker for breast cancer. The concentration of acetone in the breath of breast cancer patients has been observed to be higher than in healthy individuals. As a result, the development of sensitive, selective, and low-cost acetone sensors could offer a non-invasive pathway for breast cancer screening. Among various sensing materials, metal oxide semiconductors (MOS) have been extensively studied due to their chemical stability, tunable surface properties, and ability to detect trace levels of gases [2].

Zinc oxide (ZnO) is one of the most commonly used MOS materials for gas sensing due to its high electron mobility, wide bandgap (3.37 eV), and sensitivity to a variety of gases including acetone. However, pristine ZnO-based sensors often suffer from limited selectivity and high operating temperatures, making them less suitable for practical applications [3]. To enhance the gas-sensing performance of ZnO, metal doping has emerged as a promising strategy. Doping ZnO with noble metals such as silver (Ag) is known to create oxygen vacancies, which improves surface reactivity and lowers the operating temperature for gas adsorption and reaction [4].

Previous studies have demonstrated that Ag-doped ZnO sensors exhibit enhanced sensitivity to acetone, ethanol, and methanol due to the catalytic properties of silver. Ag-doping facilitates charge transfer between the gas molecules and the ZnO surface, increasing the adsorption sites and enhancing the sensor's response [5]. This makes Ag-doped ZnO a promising candidate for acetone sensing, particularly in applications related to breath acetone analysis for non-invasive breast cancer detection.

In this paper, we report the synthesis of Ag-doped ZnO thin films using the sol-gel method, with the goal of developing a highly sensitive and selective acetone sensor [6]. The thin films were deposited on glass substrates, followed by surface characterization and electrical measurements using a metal-semiconductor-metal (MSM) structure. The acetone-sensing performance of the Ag-doped ZnO thin films was evaluated through I-V characterization under acetone vapor exposure, with a focus on enhancing sensitivity and selectivity for breast cancer VOC detection.

II. EXPERIMENTAL DETAILS

This section details the step-by-step procedure followed in the fabrication, doping, surface characterization, and testing of Ag-doped ZnO thin films for acetone sensing [7]. The experimental procedure includes the synthesis of Ag-doped ZnO thin films via the sol-gel method, deposition of films on substrates, surface characterization, fabrication of metal-semiconductor-metal (MSM) structures, and I-V characterization under acetone vapor.

A. Synthesis of Ag-doped ZnO thin films

The Ag-doped ZnO thin films were synthesized using the sol-gel method, known for its versatility in producing uniform thin films with controlled dopant concentrations [8]. Zinc acetate dihydrate [Zn(CHCOO)·2HO], with a purity greater than 99%, was selected as the precursor material for ZnO. To prepare the precursor solution, 10.98 g of zinc acetate was dissolved in 100 mL of deionized water. Ethanol, in a 1:1 ratio, was added to the solution to act as a solvent, making the total solvent volume 200 mL [9]. The solution was stirred continuously for 30 minutes at room temperature using a magnetic stirrer until the zinc acetate was fully dissolved.

Silver nitrate (AgNO), with a purity greater than 99%, was chosen as the dopant source for silver [10]. To achieve a 1 wt% doping concentration relative to zinc acetate, 0.17 g of silver nitrate was added to the precursor solution. The dopant solution was stirred for an additional 30 minutes to ensure a homogenous dispersion of silver ions within the zinc acetate solution [11].

To initiate hydrolysis, 5 mL of monoethanolamine (MEA) was added dropwise to the prepared zinc acetate and silver nitrate solution while stirring. The solution was heated to 60°C and stirred for 1 hour to allow the formation of a transparent gel [12]. This gel was then aged at room temperature for 24 hours to complete the hydrolysis process and ensure the formation of a stable sol.

B. Deposition of thin films on substrates

Following the preparation of the Ag-doped ZnO sol, the films were deposited on glass substrates using the spin-coating method [13]. The glass substrates, measuring 2 cm × 2 cm, were thoroughly cleaned using an ultrasonic bath. Each substrate was sequentially sonicated in acetone, ethanol, and deionized water for 10 minutes to ensure the removal of contaminants, followed by drying in an oven at 100°C for 15 minutes [14].

The spin-coating process involved applying the sol-gel solution dropwise onto the cleaned glass substrate [15]. The substrate was then spun at 3000 rpm for 30 seconds in a spin coater, forming a uniform thin film. This process was repeated four times to achieve a film thickness of approximately 200 nm. After the deposition of each layer, the film was dried at 150°C for 10 minutes to remove any residual solvents and ensure uniformity before the next layer was applied.

Upon completing the spin-coating process, the coated substrates were annealed at 450°C for 2 hours in ambient air using a muffle furnace. The heating rate was controlled at 5°C/min to ensure the gradual removal of organic components from the film and to promote the crystallization of the ZnO structure [16].

C. Surface Characterization of Ag-doped ZnO Thin Films

The structural, morphological, and elemental composition of the Ag-doped ZnO thin films were characterized using multiple techniques. X-ray diffraction (XRD) was performed to investigate the crystalline structure of the thin films. The XRD measurements were conducted using a Cu K radiation source (= 1.5406 A°), scanning over a 2 range of 20°–80°. Peaks corresponding to the hexagonal wurtzite structure of ZnO were identified, and the average crystallite size was estimated using the Scherrer equation.

Scanning electron microscopy (SEM) was employed to examine the surface morphology of the films. High-resolution SEM images provided insights into the distribution of silver nanoparticles within the ZnO matrix and the uniformity of the thin films. Energy dispersive X-ray spectroscopy (EDX), integrated with SEM, was used to confirm the presence of silver and to quantify the atomic percentage of silver in the doped films, verifying the 1 wt% doping concentration [17].

Atomic force microscopy (AFM) was used to evaluate the surface roughness of the Ag-doped ZnO thin films. The root mean square (RMS) roughness was calculated to assess the influence of silver doping on the smoothness of the film surface.

D. Fabrication of MSM structure

To fabricate the MSM structure for electrical characterization, metal contacts were deposited on the Ag-doped ZnO thin films using thermal evaporation. Aluminum (Al) was chosen as the metal for the contacts due to its stability and ease of deposition. The Al contacts, with a thickness of approximately 100 nm, were deposited on the ZnO thin film under a vacuum of 10 Torr. These contacts were arranged in a parallel configuration, with a gap of 50 m between them to form the MSM structure [18].

E. I-V characterization under acetone vapor

The electrical properties of the fabricated MSM structure were analyzed through I-V characterization using a **Keithley 2614B SourceMeter**. This instrument allowed for precise control of the applied voltage and the accurate measurement of current, which is essential for evaluating the sensor's performance under acetone vapor exposure.

The MSM device was placed inside a sealed chamber to control the exposure to acetone vapor. Acetone vapor at a concentration of 100 ppm was introduced into the chamber at

room temperature. The I-V measurements were conducted by applying a voltage sweep in the range of -5 V to +5 V, with the current measured at each voltage step. The Keithley 2614B provided highly stable and reproducible measurements, which ensured the accuracy of the I-V characteristics both in the presence and absence of acetone vapor [19].

In the absence of acetone, the baseline current of the MSM structure was recorded. Once the acetone vapor was introduced into the chamber, the change in current due to acetone absorption on the Ag-doped ZnO thin film surface was measured. The sensor response S was defined as the percentage increase in current due to acetone vapor exposure and was calculated using the following equation:

$$S = \frac{I_{\text{acetone}} - I_{\text{air}}}{I_{\text{air}}} \times 100$$

where I_{acetone} is the current in the presence of acetone vapor, and I_{air} is the baseline current in ambient air. The real-time response and recovery times of the sensor were also measured. The recovery time is the time required for the current to return to 90% of the baseline value after the acetone vapor was removed from the chamber [20].

The test was repeated multiple times to confirm the repeatability of the sensor's response to acetone. The **Keithley 2614B** enabled continuous monitoring and real-time current recording during the acetone exposure and recovery cycles, allowing for the analysis of both the dynamic response and steady-state behavior of the sensor [21].

III. RESULTS AND DISCUSSION

The experimental results from this project demonstrate the sensor's effectiveness in detecting volatile organic compounds (VOCs), specifically acetone, which is significant for applications like breast cancer diagnostics [22]. The I-V characteristics and resistance measurements under different conditions reveal the sensor's high sensitivity to acetone, with clear changes in electrical conductivity and resistance when exposed to the compound [23]. These observations highlight the sensor's capability for acetone detection, supported by its dynamic response and recovery in cyclic exposures, thus confirming its potential for reliable and continuous monitoring in VOC sensing applications.

The results of this study provide detailed insights into the performance of the Ag-doped ZnO sensor in detecting acetone vapors, particularly in comparison to a vacuum environment. The key findings were derived from the analysis of I-V characteristics and resistance variations over time, which serve as indicators of the sensor's electrical behavior and its dynamic response to acetone exposure. The I-V measurements, carried out in both acetone and vacuum conditions, highlight significant differences in current levels and conductivity, suggesting the sensor's heightened sensitivity to acetone [24]. These differences are essential for

evaluating the sensor's effectiveness in detecting acetone, a key biomarker for medical diagnostics. In addition to the I-V characteristics, the dynamic response of the sensor was observed through resistance measurements over time. The sensor's response to acetone injection was marked by distinct peaks and recoveries, demonstrating both the repeatability and reliability of its performance. The ability of the sensor to consistently return to its baseline resistance after each exposure cycle underscores its potential for real-time applications, where continuous monitoring and rapid recovery are critical [25]. Furthermore, the cyclic nature of the resistance-time profile affirms the sensor's robustness and stability in detecting acetone.

Overall, the results show that the Ag-doped ZnO sensor performs well in terms of sensitivity, stability, and response time. The significant amplification of current under acetone exposure and the reproducible resistance variations indicate that this sensor has great potential for practical applications in fields like medical diagnostics, particularly for detecting acetone as a breath biomarker. These results not only validate the sensor's design but also suggest further avenues for optimization and use in other volatile organic compound (VOC) detection scenarios [7].

A. I-V Characteristics: Acetone vs. Vacuum

Fig.1 presents the I-V characteristics of the sensor in both vacuum and acetone environments. It is evident that the sensor shows a marked difference in its electrical behavior when exposed to acetone compared to the vacuum condition. The curve for acetone, represented in red, demonstrates a steeper slope compared to that in vacuum, indicating a higher current for the same applied voltage. This suggests that acetone significantly increases the conductivity of the sensor. This enhanced conductivity is crucial for the detection of acetone as it reflects a higher sensitivity of the sensor toward acetone vapor.

The I-V curve shows a near-linear behavior in both the acetone and vacuum environments at lower voltage levels, gradually shifting into a more non-linear region as the voltage increases. This non-linear behavior, especially under acetone exposure, suggests that the sensor may have undergone some form of saturation or other physical changes at higher voltages. The non-linear rise in current in the presence of acetone could be attributed to the interaction between acetone molecules and the sensing material, causing more charge carriers to become available [26].

A key observation is the amplification of current under acetone exposure. For a given voltage, the current is consistently higher when the sensor is exposed to acetone. This current amplification is crucial for VOC sensing as it confirms the sensor's ability to detect low concentrations of acetone, thus allowing for more reliable and precise detection of the target gas. This increase in current may result from the interaction between acetone molecules and the sensor surface, facilitating charge transfer processes.

The sensor exhibits a distinct behavior in the negative voltage range, where the current under acetone exposure deviates notably from that in the vacuum environment. This asymmetric response between positive and negative voltage regions indicates a potential diode-like behavior or different charge transport mechanisms at negative bias voltages. Such asymmetry may provide further insights into how acetone interacts with the sensor material at different polarities.
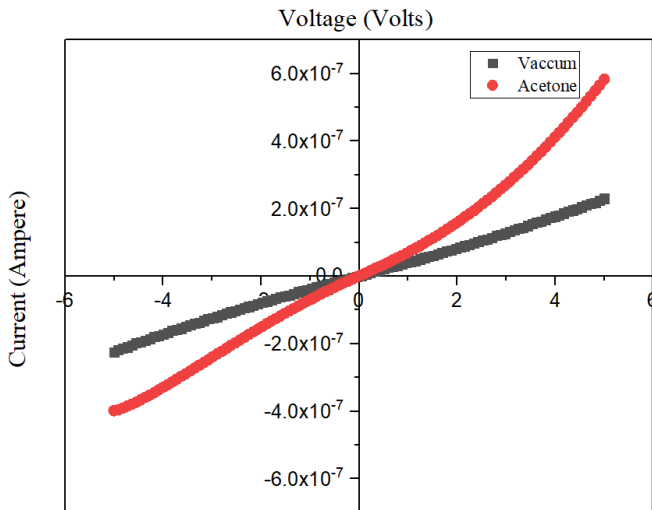

Fig. 1. I-V characteristics

B. Resistance Variation Over Time: Dynamic Response

Fig. 2 demonstrates the variation in resistance of the sensor as a function of time when exposed to a 1-microliter injection of acetone. The periodic nature of the resistance profile clearly shows the sensor's dynamic response and recovery to repeated acetone exposure. After each injection, the resistance rises and falls in a cyclical manner, reflecting the sensor's consistent and repeatable response to acetone. The peaks in resistance after each acetone exposure illustrate that the sensor effectively captures the presence of acetone, and the return to baseline indicates successful recovery.

The sensor's ability to return to its initial resistance state after each exposure cycle highlights its stability and repeatability in detecting acetone. Each cycle shows similar peaks and troughs, confirming that the sensor does not suffer from significant drift or hysteresis over time. This repeatability is essential for practical applications in real-time gas sensing, where the sensor needs to consistently detect changes in VOC concentration without degradation in performance [7].

From the resistance-time graph, it is also apparent that the sensor is highly sensitive to small acetone concentrations. The clear changes in resistance following each acetone exposure confirm the sensor's high sensitivity. This sensitivity is vital for applications such as breath analysis for medical diagnostics, where detecting trace amounts of acetone could indicate conditions like diabetes or breast cancer. The sharp response and recovery demonstrate that even minute amounts of acetone can be detected reliably.

The sensor's recovery time—indicated by how quickly the resistance returns to its baseline after acetone exposure—is relatively short. This fast recovery suggests that the sensor could be used in dynamic environments where continuous monitoring is required. A short recovery time is desirable as it ensures the sensor can be reused quickly for subsequent measurements without lengthy delays. Additionally, the sensor shows a broad dynamic range, as it can detect both the initial exposure and subsequent recoveries effectively [28].
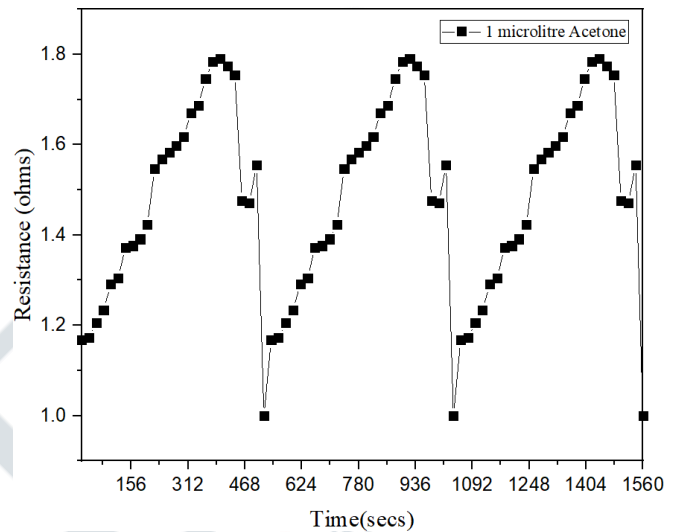

Fig. 2. Resistance plot

In conclusion, the data from these two graphs reveal that the sensor effectively detects acetone by demonstrating a clear and measurable response in both its I-V characteristics and resistance behavior. The significant shift in current and the cyclic variation in resistance validate the sensor's potential for acetone detection, with applications in VOC sensing for breast cancer diagnostics. Moreover, the sensor's ability to maintain performance over multiple exposure cycles further underscores its viability for real-time, repeated use in practical applications. The results from the I-V and resistance-time graphs demonstrate that the sensor has excellent potential for acetone VOC detection. Its high sensitivity, stable response, and fast recovery times make it an ideal candidate for applications in medical diagnostics and environmental monitoring. The significant difference in the sensor's performance between acetone and vacuum conditions, along with its consistent cyclic behavior, underscores its robustness and reliability as a VOC sensor. These characteristics position the sensor as a promising tool for real-time acetone monitoring in practical applications.

IV. CONCLUSION

In conclusion, the results from the I-V and resistance-time graphs demonstrate that the sensor has excellent potential for acetone VOC detection. Its high sensitivity, stable response, and fast recovery times make it an ideal candidate for applications in medical diagnostics and environmental

monitoring. The significant difference in the sensor's performance between acetone and vacuum conditions, along with its consistent cyclic behavior, underscores its robustness and reliability as a VOC sensor. These characteristics position the sensor as a promising tool for real-time acetone monitoring in practical applications.

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