Influence of Al Doping on the Morphological, Structural and Gas Sensing Properties of Electrochemically Deposited ZnO Films on Quartz Resonators

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Abstract: The detection of hazardous gases at different concentration levels at low and room temperature is still an actual and challenging task. In this paper, Al-doped ZnO thin films are synthesized by the electrochemical deposition method on the gold electrodes of AT-cut quartz resonators, vibrating at 10 MHz. The average roughness, surface morphology and gas sensing properties are investigated. The average roughness of Al-doped ZnO layers strongly depends on the amount of the doping agent Al2(SO4)3 added to the solution. The structural dependence of these films with varying Al concentrations is evident from the scanning electron microscopy images. The sensing properties to ethanol and ammonia analytes were tested in the range of 0–12,800 ppm. In the analysis of the sensitivity to ammonia, a dependence on the concentration of the added Al2(SO4)3 in the electrochemically deposited layers is also observed, as the most sensitive layer is at 3 × 10−5 M. The sensitivity and the detection limit in case of ammonia are, respectively, 0.03 Hz/ppm and 100 ppm for the optimal doping concentration. The sensitivity depends on the active surface area of the layers, with those with a more developed surface being more sensitive. Al-doped ZnO layers showed a good long-term stability and reproducibility towards ammonia and ethanol gases. In the case of ethanol, the sensitivity is an order lower than that for ammonia, as those deposited with Al2(SO4)3 do not practically react to ethanol.

Keywords: electrochemical deposition; Al-doped ZnO; gas sensor; characterization; gas sensing; ammonia; ethanol

1. Introduction

Air pollution in big cities and the attendant deterioration of the quality of life urge the development of accurate environment monitoring systems. Gas sensing is an important part of these platforms and many sensor devices based on various principles of analyte signal transduction have been researched, developed and applied [1–7].

Metal oxide nanomaterials have received a lot of attention in gas sensor fabrication due to their relatively easy controlled synthesis, diversity of surface morphology and grain size, and high sensing performance, especially good sensitivity, selectivity, and fast response and recovery time [6].

Among the various semiconductors, metal oxide ZnO is one of the most widely investigated due to its attractive properties, such as nontoxicity, excellent optical absorption, high exciton binding energy and long electron lifetime [8–10]. Moreover, ZnO is a material with high electron mobility and great intrinsic impurities, which may cause increased
ZnO nanostructures have the ability to form highly active surface areas [11]. They are widely used as gas-sensing materials with good thermal stability [10].

Different methods (sol–gel, chemical vapor deposition, electrospinning, etc.) have been applied for the synthesis of ZnO nanostructures with various sizes, morphologies and gas sensing properties [12]. In order to increase sensitivity, different effective solutions, such as metal doping, functionalization with noble metal nanoparticles, UV activation, inclusion of carbonaceous nanostructures, e-beam irradiation, have been proposed [12]. Many efforts have been devoted to the synthesis methods with various doping agents [10,12,13]. Transition metals, such as Ni, Co, Fe and Cu, have been reported as dopants in ZnO nanostructures [14,15]. Dopants are used to improve the sensitivity and selectivity of the sensor, to accelerate the response towards the target gas by changing the morphology and energy band structure, as well as to increase the surface-to-volume ratio and thus to create more interaction centers on the metal oxide semiconductor structure [10,12,13]. The dopants may also increase the stability and reduce the working temperature of sensor devices [12].

It is known that doping with Al can improve the sensitivity and conductivity of ZnO nanomaterials and accelerate chemical reactions in the gas sensor [13]. Al dopants can enhance the oxygen adsorption capacity, which may increase the gas interaction centers [13]. Al$^{3+}$ can effectively substitute Zn$^{2+}$ in the crystal lattice on account of its smaller ionic radius ($r_{\text{Zn}} = 0.074$ nm, $r_{\text{Al}} = 0.054$ nm) [13,16,17].

Different techniques have been used for preparing Al-doped ZnO thin films on various substrates. The preparation of Al-doped ZnO nanorods grown on a glass substrate and annealed under hydrogen atmosphere has been discussed by Zhong et al. [18]. Pure and Al doped ZnO films were prepared by the pulsed laser deposition technique for optical gas sensor application [19]. Al-doped ZnO nanoparticles have been synthesized by the sol-gel method and the enhancement of sensitivity to ammonia has been detected [20]. A narcissus-like Al-doped ZnO nanostructure was synthesized via a one-pot hydrothermal method in [21]. Gas sensing tests revealed the enhanced sensing response to NO$_2$ of the doped structure compared with those of pure ZnO [21]. Vattappalam et al. [22] reported the synthesis by successive ionic layer adsorption and reaction method of Al-doped ZnO thin films, which can be used as fast-response sensors for ethanol vapors.

An important part of the sensing platforms is their fabrication by environmentally compatible and cost-effective technologies. In our work, we use the known advantages of the electrochemical deposition method [23] to study the influence of Al doping on morphological and structural properties of nanostructured ZnO:Al films, namely its environmental compatibility in line with the ability for coating large surface areas with controlled and patterned growth of diverse morphology and size nanostructures. In order to upgrade the potential of this method in producing layers with improved sensing abilities at room temperature conditions, we used a quite simple and highly sensitive method for direct mass measurement—quartz crystal microbalance (QCM). The QCM technique based on quartz thickness shear mode resonators with active layer has been widely explored for many gas sensing applications. The working principle is based on resonance frequency shifts produced from the mass change of a sensitive layer due to gas adsorption [24–27].

We chose as analytes ammonia and ethanol vapors—gases with different reductive properties. Ammonia (NH$_3$) has many applications in the industry and its detection at different concentration levels at room temperature is a challenging task [13]. Furthermore, the detection of NH$_3$ is of great importance because of its toxicity when inhaled during long-term exposure at an unsafe level [13,28].

2. Materials and Methods

The deposition of ZnO layers on the electrodes (gold) of quartz resonators was performed by an electrochemical process using a three-electrode electrochemical system. A negative potential of 900 mV was maintained between the saturated calomel electrode (acting as a reference electrode) and the cathode (on which the sample is located). The
nanostructures were formed at temperature 70 °C and deposition time of 15 min from aqueous electrolyte containing ZnCl$_2$—$5 \times 10^{-3}$ M, KCl—0.1 M and Al$_2$(SO$_4$)$_3$—from 0 M to $4 \times 10^{-3}$ M. The thickness of the ZnO layers, the concentration of the dopant Al and the surface morphology were controlled by changing the following parameters (deposition potentials, temperature, Al$_2$(SO$_4$)$_3$ concentration and plating time) in the electrochemical system.

The study on the gas sensing properties of the Al-doped ZnO (ZnO:Al) layers deposited by electrochemical technology was performed using the quartz crystal microbalance (QCM) method. The AT-cut resonators (Novaetech, Pompei, Italy) with gold electrodes were fabricated to operate at a fundamental frequency of 10 MHz. The studied quartz resonators had a diameter of 14 mm and a thickness of 200 µm. The upper and lower electrodes had diameters of 12.2 and 6.4 mm, respectively, and the electrochemical layers of ZnO:Al were deposited on the large electrode. The design of the resonators with deposited electrochemical ZnO:Al films is presented in Figure 1.

**Figure 1.** Configuration of the location of the gold electrodes and the electrochemically deposited ZnO:Al layer on the quartz resonator.

The exposure to chemical vapors was realized in a homemade non-flow system containing a measuring box with a volume of 22.5 L, and based on the evaporation of the concentration proportional quantities of liquid analyte (Figure 2).

**Figure 2.** Box for organic compound gas measurements.

The liquid was injected through a hermetic inlet in the box by a syringe in steps of defined quantities (0.1 mL). For the homogenous distribution of the resulting air–gas
mixture, a fan was used. After each experiment, the resonator surface was submitted to ambient atmosphere by opening the upper wall of the cell. Each new portion of analyte was added at the end of a relaxation interval when the system achieved an approximate state of equilibrium. The quartz crystal resonator was mounted vertically by the holder. The resulting change of the resonant frequency and the temperature in the camera were monitored and the data were displayed on a computer by QCM Arduino Shield (Novaetech, Pompei, Italy). The working temperature was maintained at 25 °C and was controlled within 1 deg during the experiments.

The resonator surface with ZnO:Al films was exposed to the action of ammonia and ethanol vapors. Exposure to analyte caused absorption of gas molecules resulting in a change of the resonant frequency due to the mass loading effect. The concentration data (in mL) were converted to ppm using a scheme similar to that reported in [29]. We used the well-known fact that 1 mol of ideal gas has a volume of 22.4 L at room temperature and atmospheric pressure. From the density of the liquid analyte and its molar mass, the molar content of the analyte was calculated, as well as the corresponding volume and the ratio of this volume to the volume of the measurement cell (22.5 L). After stopping the supply of volatile substances into the chamber, the resonators returned to their initial frequencies relatively slowly. The recovery time depends on the conditions, temperature and humidity, but slowly (about 24 h). If resonators are heated, the recovery time is significantly reduced.

3. Results and Discussion

The determination of the morphological properties of the electrochemical ZnO:Al layers deposited on the quartz resonators was performed by optical profilometry and scanning electron microscopy (SEM). The 3D images of the ZnO layers with different concentrations of Al₂(SO₄)₃ are shown in Figure 3 and the results related to the calculations of the average roughness are presented in Table 1.

![3D images of electrochemical ZnO layers](image)

Figure 3. 3D images of electrochemical ZnO layers, deposited with different concentrations of Al₂(SO₄)₃: (a) 0 M; (b) 1 × 10⁻⁵ M; (c) 2 × 10⁻⁵ M; (d) 3 × 10⁻⁵ M; and (e) 4 × 10⁻⁵ M.

To determine the average roughness of the layers, measurements were made in several different sections (with an area of 97 µm × 71 µm) from the surface of the sample. The results show that, with the increase in the concentration of Al₂(SO₄)₃ from 0 M to 4 × 10⁻⁵ M, there is an increase in the average roughness of the deposited layers. This increase is due to the change in the morphological structure (Figure 4) of the layers. For comparison, Table 1 shows also the average roughness of the quartz resonator, which is much smaller than that of the layers deposited on it and does not affect the roughness results. The indices 1, 2, and 3 (in Table 1) for Sq mean the corresponding number of the analyzed section.
Table 1. Average roughness of the ZnO layers deposited with different concentrations of Al$_2$(SO$_4$)$_3$.

| Concentration of Al in Layers | Quartz Resonator | Electrochemical ZnO |
|-------------------------------|------------------|---------------------|
|                               | Sq–1 (nm)        | 22.9                |
|                               | Sq–2 (nm)        | 24                  |
|                               | Sq–3 (nm)        | 22                  |
| AVG (nm)                      | 23 ± 0.7         |
|                               | 0 M              | 65                  |
|                               | 1 × 10$^{-5}$ M  | 106.6               |
|                               | 2 × 10$^{-5}$ M  | 181.3               |
|                               | 3 × 10$^{-5}$ M  | 235.9               |
|                               | 4 × 10$^{-5}$ M  | 379                 |
|                               | 3 × 10$^{-5}$ M  | 0.80                |
|                               | 5 M              | 0.48                |
|                               | 2 × 10$^{-5}$ M  | 0.09                |
|                               | 3 × 10$^{-5}$ M  | 0.38                |
|                               | 4 × 10$^{-5}$ M  | 0.23                |
|                               | 5 M              | 0.04                |

SEM micrographs of ZnO:Al layers with different concentrations of Al$_2$(SO$_4$)$_3$ deposited by the electrochemical method are shown in Figure 4. The micrographs show that in the layers deposited without Al$_2$(SO$_4$)$_3$ in the solution we have “nano-rods” with a hexagonal shape tightly located on the surface (Figure 4a). When Al$_2$(SO$_4$)$_3$ is added to the solution, we observe the appearance of “nano-walls” in the structure. As the concentration of Al$_2$(SO$_4$)$_3$ in the solution increases, the density of the “nano-rods” located on the surface of the layers decreases (Figure 4b–d), while the dimensions of the “nano-walls” increase (from 2–5 µm in Figure 4b to 5–10 µm in Figure 4d,e). The layer deposited at a concentration of Al$_2$(SO$_4$)$_3$ $4 \times 10^{-5}$ M is formed mainly as “nano-walls”. The probable reason for the change in the morphology (from nano-rods to nano-walls) of the layers is the increased concentration of aluminum in them (Table 2), which makes the deposition of one type of structure more energetically advantageous than others. The results for aluminum percentage in the layers obtained by EDX analysis are shown in Table 2. The data presented show a linear relationship between the increase in the concentration of Al$_2$(SO$_4$)$_3$ in the solution and the increase in the amount of aluminum in the layers.

![Figure 4. SEM images of ZnO layers, electrochemically deposited with different concentrations of Al$_2$(SO$_4$)$_3$: (a) 0 M; (b) $1 \times 10^{-5}$ M; (c) $2 \times 10^{-5}$ M; (d) $3 \times 10^{-5}$ M; (e) $4 \times 10^{-5}$ M.](image-url)
Table 2. EDX analysis for Al concentrations in electrochemically deposited ZnO layers with different concentrations of Al$_2$(SO$_4$)$_3$.

| Concentration of Al$_2$(SO$_4$)$_3$ in Solution | Concentration of Al in Layers | Atom. (%) | Wt. (%) | Error. (%) |
|-----------------------------------------------|-----------------------------|-----------|---------|----------|
| 0 M                                           |                             | 0         | 0       | 0        |
| $1 \times 10^{-5}$ M                          | 0.13                        | 0.08      | 0.02    |
| $2 \times 10^{-5}$ M                          | 0.38                        | 0.23      | 0.04    |
| $3 \times 10^{-5}$ M                          | 0.80                        | 0.48      | 0.09    |
| $4 \times 10^{-5}$ M                          | 1.07                        | 0.65      | 0.1     |

The mass ($\Delta m$) of the electrochemical ZnO:Al layers deposited on the larger electrode of the quartz resonators was calculated according the Sauerbrey equation [25]:

$$\Delta f = \left( -\frac{2F_0^2}{A\sqrt{\rho q\mu q}} \right) \Delta m$$

where $\Delta m$ is the mass change (g); $F_0$ is the resonant frequency (Hz) of the fundamental mode; $\rho_q$ is the density of quartz ($\rho_q = 2.648$ g/cm$^3$); $\mu_q$ is the shear modulus of quartz for AT-cut crystal ($\mu_q = 2.947 \times 10^{11}$ g·cm$^{-1}$·s$^{-2}$); $A$ is the active piezoelectrical crystal area (cm$^2$); and $\Delta f$ is the QCM frequency change (Hz). The results are presented in Table 3. The calculations show that the layer deposited without Al$_2$(SO$_4$)$_3$ in the solution has a significantly smaller frequency difference $\Delta f = F_0 - F$ ($F_0$ is the initial resonant frequency of the resonator and $F$ is the frequency after film deposition). That means less accumulated mass $\Delta m$ than the mass of the layers deposited with Al$_2$(SO$_4$)$_3$. In the doped layers (those with Al$_2$(SO$_4$)$_3$), we have relatively similar results for the frequency difference $\Delta f$, which indicates that there is no relationship between the increase in the concentration of Al$_2$(SO$_4$)$_3$ in the solution and the mass accumulated in the layers.

Table 3. Calculated mass ($\Delta m$) of the electrochemical ZnO:Al layers deposited on the larger electrode of the quartz resonators.

| Conc. of Al$_2$(SO$_4$)$_3$ | $F_0$, Hz | $\Delta f$, Hz | $\Delta m$, g |
|-----------------------------|-----------|----------------|--------------|
| 0 M                         | 10,007,464| 5020           | 7.12 $\times 10^{-6}$ |
| $1 \times 10^{-5}$ M        | 10,005,805| 15,037         | 2.13 $\times 10^{-5}$ |
| $2 \times 10^{-5}$ M        | 10,008,952| 13,276         | 1.88 $\times 10^{-5}$ |
| $3 \times 10^{-5}$ M        | 10,007,835| 12,700         | 1.81 $\times 10^{-5}$ |
| $4 \times 10^{-5}$ M        | 10,005,734| 12,932         | 1.84 $\times 10^{-5}$ |

The plots of data used for analysis of layers sensing properties to ethanol and ammonia are presented on Figure 5. The observed first response time was about 4 to 6 s after probe insertion and it depends on the liquid probe delivered into the measurement box. We took data at the time of reaching equilibrium for the mutual processes of analyte evaporation and its adsorption–desorption rate on the hybrid films. The time for reaching equilibrium, needed for making consecutive measurements was from 10 to 15 min. In the case of ethanol (Figure 5a), the layers deposited with Al$_2$(SO$_4$)$_3$ in the solution did not show any sensitivity, while the one deposited without Al$_2$(SO$_4$)$_3$ showed a relatively small frequency deviation (about 30 Hz). The graphs for the ammonia frequency study are shown in Figure 5b, in which it is observed that the layers containing Al$_2$(SO$_4$)$_3$ in the solution show a bigger frequency change at lower concentrations (to 5000 ppm). It is known that the gas sensing mechanism of ZnO nanostructures relies on the adsorption of oxygen molecules on their surface in the presence of atmospheric air. As a consequence of the high electronegativity of oxygen molecules and due to the extraction of electrons from the conduction band of ZnO, the formation of oxygen ions occurs [13]. When NH$_3$ molecules interact with the sorbed...
oxygen ions, they oxidize to N\textsubscript{2}, H\textsubscript{2}O, and an electron. The interaction can be described as follows \cite{13, 30}:

\[
4\text{NH}_3 + 3\text{O}_2^-(\text{ads}) \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} + 3e^- 
\]

In case of ethanol, the gas may undergo different reactions with two routes of decomposition (dehydration and dehydrogenation) \cite{31}:

\[
\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \text{ acidic oxide}
\]

\[
2\text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{CH}_3\text{CHO} + \text{H}_2 \text{ basic oxide}
\]

These primary products are consecutively oxidized:

\[
\text{C}_2\text{H}_4 + 3\text{O}_2^-(\text{ads}) \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 6e^- 
\]

\[
2\text{CH}_3\text{CHO}(\text{ads}) + 5\text{O}_2^-(\text{ads}) \rightarrow 4\text{CO}_2 + 4\text{H}_2\text{O} + 10e^- 
\]

Gas sensing may be improved by doping because of the high surface area of small-sized particles, which further increases the number of chemisorbed oxygen ions. Moreover, Al doping in ZnO produces point defects and thus modifies the surface. Obviously, Al-doped ZnO samples, due to their higher donor content, contain more O\textsubscript{2} species than the undoped ones. The substitution of Zn\textsuperscript{2+} ions with Al\textsuperscript{3+} is effective because the ionic radius of Zn\textsuperscript{2+} is greater than that of Al\textsuperscript{3+} \cite{13}. It is known that the increase in Al dopant concentration usually leads to morphology changes and the deterioration of the deposited layers \cite{23}. As the Al concentration increases, the shape, size and distribution of the particles in the layer also start to affect the sensitivity, and those with a more developed surface also have a higher frequency change. These layers contain more centers for gas adsorption and their sensitivity is greater because of the higher probability of interaction with gas molecules. The layer deposited with \(3 \times 10^{-5}\) M of Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} has the best frequency change, as it contains “nano-walls” and “nano-rods”, whose shape and size probably contribute to a better interaction with ammonia molecules (Figure 4). The linear parts of the plots in Figure 5 can be used for estimation of sensitivity. As a measure of detection limit, the approach justified in \cite{32} can be used, namely three times the concentration level that corresponds to the short time stability of oscillator device. Calculated by this method, the sensitivity and the detection limit in case of NH\textsubscript{3} are, respectively, 0.03 Hz/ppm and 100 ppm at the shown optimal doping concentration of \(3 \times 10^{-5}\) M. Based on the found optimal doping concentration, these parameters could be significantly improved by the variation of deposition parameters (time and temperature), as well as other known approaches. For Al-doped ZnO thin films in \cite{33} and in \cite{34}, the reported response for ammonia is 100 ppm at room temperature and 25 ppm at 100 °C, respectively. The difference in sensitivity between ethanol and ammonia is due to the significantly higher binding energy of ammonia to ZnO (14.6 eV) than that of ethanol to ZnO (3.2 eV) \cite{35}. The resonators with the studied ZnO:Al layers were tested every 30 days for 3 months. No changes of the working parameters were observed which is indication for long-term stability of the electrochemical metal oxide layers.
The obtained results reveal that these ZnO:Al coatings produced by electrochemical preparation successfully combine the advantages of the electrochemical method and the quartz microbalance technique.

**4. Conclusions**

The results on the morphological, structural and gas sensing properties of electrochemically ZnO films deposited at different concentrations of Al₂(SO₄)₃ on quartz resonators are reported. The data from the calculations show that the average roughness of the electrochemical layers increases with the increase in Al₂(SO₄)₃ in the solution, and this dependence is linear. The relationship between the concentration of Al₂(SO₄)₃ in the solution and the aluminum content in the layers is also linear. SEM micrographs show a strong influence between the size and shape of the particles in the layers and the concentration of Al₂(SO₄)₃, as from particles in the form of “nano-rods” the layers pass into those containing mainly “nano-walls”. The calculations for accumulated mass (Δm) of the electrochemical ZnO:Al layers shows that there is no connection between the increase in the concentration of Al₂(SO₄)₃ in the solution and the mass accumulated in the layers. The sensitivity of the layers depends mainly on their developed surface, as those deposited with Al₂(SO₄)₃ show better selectivity (because they do not react to ethanol) and sensitivity at low ammonia concentrations. Based on the found optimal doping concentration, the sensitivity and the detection limit could be significantly improved by the variation of deposition parameters. The obtained results reveal that these ZnO:Al coatings produced by electrochemical deposition could be profitably used for precise ammonia sensors working at room temperature conditions. Such sensors based on metal oxide layers successfully combine the advantages of the electrochemical method and the quartz microbalance technique.

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