Connected AZO Nanorods for Sensitivity Enhancement of Chemical Sensors at Room Temperature

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Abstract: In this work, the vertically aligned, high conductive Al-doped ZnO nanorod thin film was prepared by multi-layers grown method in solution process. This method of connected nanorod structure is unique of its kind compared with existing hydrothermal process for preparing nanorod. The diameter of AZO nanorod is around 14~16nm with [002] preferred orientation. The Hall measurement indicates the AZO nanorod exhibits high layer conductivity of 280 S/cm. The XPS characterization indicates that the AZO nanorod annealed in forming gas contain high percentage of non-binding oxygens that is suitable for sensor application. The sensing performances of the synthesized nanorod thin film towards the detection of oxidizing agents were analyzed by the current (I)–voltage (V) characteristics in room temperature. With high surface area, the AZO shows sensitivity of 72%, 1660%, and 4.34 x10^6% for H_2O_2, ethanolamine and acetic acid, respectively. 1.02 μM (S/N=3) is the detection limit with broad range of 0.015mM to 29mM is demonstrated for sensing H_2O_2.

Keywords: AZO, nanorod structure, solution process, Chemical sensor, room temperature sensing.

1. Introduction

The extensively used oxidizing agent in the food, bioanalysis and pharma industries is H_2O_2. It is also used as an indispensable mediator in medical diagnosis and aqueous bio-sensing [1–3]. For accurate determination of H_2O_2, a reliable sensing material for monitoring its presence is significant in the sensor research domain. Though electrochemistry[4] is the popular among for its detection, bio-physical fluorescence [5], mass to charge ratio spectrophotometry [6], and chemiluminescence [7], are also used for the same. In real time applications, transition metal oxide materials are employed for detecting chemical/gas widely. 1D metal oxide semiconductor (MOS) nanostructure thin films with ‘n’ type conductivity like CdO [8], ZnO[9], SnO_2[10] are employed. Doping leading to ‘p’ type as in TiO_2 [11], or transparent WO_3[12], or high mobility graphene [13] are being used for organic compound detection. These materials show great variation in electrical conductivity towards surface oxygen species. Though electrochemical sensing of H_2O_2 through nanostructured ZnO by electrodeposition [14] have been incorporated, metal doped ZnO structures especially using solution process for detecting H_2O_2 is very less studied. Growing connected nanorod structure in the solution process as proposed in this paper is unique of its kind compared with existing electrochemical and physical deposition techniques [15]. In this study, Al-doped ZnO nanorod were synthesized using solution process, characterized and tested its sensing behavior for oxidizing agents. Detail analysis for H_2O_2 in room temperature is presented in this paper.
2. Materials and Methods

2.1. Experimental detail

Zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O, 99.9% sigma Altrich) was dissolved with 1 at.% doping concentration of Al(NO₃)₃·9H₂O/AlCl₃·6H₂O (99.9% sigma Altrich) added to the anhydrous ethanol. Ethanolamine was added dropwise to the mixture at a concentration of 0.1M. The precursor solution was refluxed for 12 hours and then kept overnight for aging. Using acetone the glass substrate was cleaned initially, following it rinsed in a sonic bath by deionized water. The solution was spin-coated at 4500 rpm for 30 sec and each coating was annealed for a temperature at 400°C for 10 min. The coating and heat treatment process was repeated for ten times. The set of samples with AlCl₃ as precursor coined as condition 1 and samples with Al(NO₃)₃ as precursor are termed as Condition 2. Both types are annealed under 500°C for 1 hour in forming gas (5% H₂ and 95% N₂).

2.2. Measurement detail

Investigation of crystallinity and phase composition of the films after annealing were done using an X-Ray diffractometer (λ=1.5418Å) with Cu Kα radiation) with the scanning range between 20 and 80°. Surface morphology of the films examination was carried out using FESEM, JSM-6700; JEOL Co., Tokyo, Japan. Cross-sectional FESEM images were used to measure the thickness of the AZO films. Ultraviolet visible spectrometer (Thermo scientific, Evolution 220) was used to measure the UV–Vis absorption spectra. Hall Effect measurements technique (Napson, RT70/RG-5, Japan) ensured the electrical characterization of the film. Further chemical analysis, was analyzed by XPS, (ULVAC-PHI PHI 5000 VersaProbe- Al Ka radiation)

2.3 Sensor fabrication and measurement

The AZO thin film sensor device was fabricated on a 20 mm ×10 mm glass substrate. Following the thin film deposition, two Ag electrode contacts (4 mm × 4mm) was deposited on the top of the sensing AZO layer as shown in figure1. The Ag electrodes were thermally evaporated (vacuum pressure~ 2x10-6 Torr) with a thickness of 50nm.

![Figure 1. Schematic of AZO based planar sensor device](image)

Uniformity of the sensing area was accomplished by, encapsulating the thin film using silica gel and a PET film with the hole (dia-5mm). The current-voltage (I-V) characteristics and changes in resistance due to different solute of the sensing device were measured by an Agilent 2192A analyze for analyzing semiconductor parameters. Thin films in this study, was continuously irradiated using an ultraviolet-light emitting diode 365-nm (UV-LED) at room temperature (25°C, relative humidity...
When dynamic equilibrium due to electron–hole pair generation and recombination in the thin film is reached, the sensing surface was exposed to different solute concentrations. The sensitivity of the nano AZO film was tested by using the thin film to detect different types of solutes (H$_2$O$_2$, Ethanolamine and Acetic acid) in the concentration range from 14.6μM to 0.0293M. The sensitivity to the H$_2$O$_2$ in this paper is calculated from the film resistance in air (Ra) and the resistance of film in the presence of test solute (Rg) which in total defined by S= [(Rg-Ra)/Ra]*100%. The time to reach 90% of the saturation, is the response time and fall from 90% of its corresponding is the recovery time.

3. Results and discussion

The AZO thin films shows matching XRD pattern as shown in figure 2 with ([JCPDS] no. 36-1451) i.e the ZnO diffraction pattern, with no trace of Al$_2$O$_3$. Polycrystalline nature was observed for both the films with preferred (002) plane and the intensity is related to the choice of dopant for the samples. The line broadening from the XRD diffraction pattern was sued to calculate the AZO thin film crystallite size. The AZO thin film crystallites (D) size an important parameter in morphology examination is calculated from the Scherrer equation,

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where D represents the average dimension of the crystallites and $\beta^2 = B^2 - b^2$ defines the crystallite size $\beta$. Full width at half maximum (FWHM) of the peak (B), instrumental factor (b = 0.13) are used to derive the crystallite size.

![XRD pattern](image)

Figure 2. Structural characterization of AZO connected nanorod film for condition 1 and 2.

The calculated grain sizes of the prepared AZO films are listed in table 1. Samples in condition-2 has better (002) orientation i.e. with nitrates as dopants. To understand the post annealing treatment effects on different precursor on AZO films for sensing property is further investigated. The condition-1 AZO thin film crystallinity found decreased compared to its counterpart.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Post annealing</th>
<th>2θ (002)</th>
<th>FWHM (degree)</th>
<th>Grain size (nm)</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
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<tr>
<td>Condition 1</td>
<td>Forming gas*</td>
<td>34.54</td>
<td>0.47</td>
<td>18.5</td>
<td>65.6</td>
</tr>
<tr>
<td>Condition 2</td>
<td></td>
<td>34.52</td>
<td>0.39</td>
<td>22.3</td>
<td>68.4</td>
</tr>
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</table>

*5% H$_2$ and 95% N$_2$
It is noteworthy that the angular peak position (2θ) of condition-1 sample which corresponds to the ZnO (002) diffraction peak is shifted to smaller angle. Under reduced atmosphere annealing condition, both the samples shows compressive strain on the films as reported [16]. Polycrystalline films annealed in oxygen free environment at high temperature concludes the similar behavior with proposed zone model [17]. Accordingly, segregation of impurities taking place at the grain boundaries of the film results in reduced grain size, which predominantly depends on the precursor chosen proves with the results.

![Condition 1](image1.png)

![Condition 2](image2.png)

**Figure 3.** Morphological characterization top view, cross section and its schematic illustration of the AZO film in condition 1 (a,b,c) and condition 2 (d, e, f), respectively.

FESEM image in figure 3 reveals the structure of solution processed AZO thin film. Average nanoparticle size of the thin film AZO was figured out from the FESEM image in both condition as 18-22nm. Morphology difference of the films is well indicated in the FESEM images, which unfold that precursor chosen along with the tuned parameters mainly affected the film. The nanorod structure in condition 1 is evident due to the Al cl dopant (figure 3b). The granular structure for the precursor Al Ni for condition 2 is revealed in figure 3e. The forming gas annealing environment affects the carrier concentration of the films, but also an impact on the grain size, this is pretty evident in figure 3a and d. The nanorod structure of AZO in condition 1 precursor chosen along with the tuned parameters have sufficient reaction area yielded by higher surface-to-volume ratio, compared to condition 2 film (as shown in figure 3c and 3f) thereby helps in sensing chemicals.

### 3.1. Electrical properties

The films made from different dopants annealed in the forming gas environment shows different levels of surface adsorbed oxygen. But for the purpose of comparison on same ground this specific sample types were chosen. The relative intensity of each oxygen component for the AZO thin films for this paper is calculated from XPS is shown in table 2. The XPS spectra for AZO films relating with O 1s peaks on the surface of samples for different conditions can be fitted by three near Gaussians, each one centered at (O₁) 530.06±0.03, (O₂) 531.56±0.05, and (O₃) 532.62±0.12 eV as in figure 4.
The lower binding energy peak at (530.3 eV) assimilates to lattice oxygen of AZO[18]. Adsorbed hydroxyl group on surface is related by binding energy (532.3 eV). It also accounts for adsorbed O\_2 species, which are in chemisorbed form on the AZO surface [19]. The result shows that high binding energy component (O\_III) for both types of AZO films irrespective of the dopants annealed in the forming gas environment has the highest values.

### Table 2. Relative Strength from O 1s spectrum of AZO film

<table>
<thead>
<tr>
<th>Samples</th>
<th>O_I/(O_{Total})</th>
<th>O_II/(O_{Total})</th>
<th>O_III/(O_{Total})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition 1</td>
<td>12.30</td>
<td>33.29</td>
<td>54.39</td>
</tr>
<tr>
<td>Condition 2</td>
<td>7.374</td>
<td>32.09</td>
<td>60.53</td>
</tr>
</tbody>
</table>

Conductivity, concentration and mobility of the AZO film due to majority carriers were confirmed by the Hall-effect measurement. It confirms the n-type conductivity of the film and affirms a bulk carrier density of $4.10 \times 10^{20}$ cm\(^{-3}\); hall mobility of 4.26 cm\(^2\)/V.s and resistivity of $3.52 \times 10^{-2}$ Ωcm for samples in condition 1. The similar approximation was achieved for the samples in condition 2 in which bulk carrier density, hall mobility, and resistivity are $4.32 \times 10^{20}$ cm\(^{-3}\), 4.01 cm\(^2\)/V.s and $3.60 \times 10^{-2}$ Ωcm respectively. Henceforth conductivity of the thin film remains the same irrespective of the dopants when processed in the same condition.

### 3.2. Sensor properties

To understand the principle of sensitivity to this AZO film as a sensor, AZO thin film made from different dopants was chosen to compare its characteristics. The sensitivity of the AZO sample annealed in forming gas to chosen solutes in the room temperature are shown in figure 5. The sensitivity of the AZO was high as 72% for H\_2O\_2, 1660% for Ethanolamine, 4.34E6% for Acetic acid at 0.015M for all solute.
Figure 5. Sensitivity of AZO thin film vs concentration of (a) H$_2$O$_2$, (b) Acetic Acid, (c) Ethanolamine, (d) Methanol, (e) Acetone.

Notably, acetone and methanol has very low sensitivity 2.8% and 8.3% respectively. Its corresponding comparison chart is also given in figure 6. To study the sensing mechanism in the nano AZO film, the dynamic response of (condition 1 and condition 2) AZO thin film sensor at room temperature detection with increasing concentration of H$_2$O$_2$ (0.015mM to 29mM) was analyzed and its response is displayed in figure 7. The resistance of the film initially increases after the introduction of H$_2$O$_2$ solute and later reaches saturation, is revealed in the plot. The resistance decreases and returns to its initial value after the H$_2$O$_2$ feed is withdrawn gently.

Figure 6. Histogram for the sensitivity of AZO thin film for various chemical concentrations.

Figure 7. Changes in electrical resistance of AZO thin film towards different concentrations of H$_2$O$_2$: (a) condition 1 (b) condition 2.
To study the sensing mechanism in the nano AZO film, the dynamic response of (condition 1 and condition 2) AZO thin film sensor at room temperature detection with increasing concentration of H$_2$O$_2$ (0.015mM to 29mM) was analyzed and its response is displayed in figure 7. The resistance of the film initially increases after the introduction of H$_2$O$_2$ solute and later reaches saturation, is revealed in the plot. The resistance decreases and returns to its initial value after the H$_2$O$_2$ feed is withdrawn gently.

The extent of adsorption and desorption determines the sensitivity of metal oxides. Sensitivity in turn determined by the nanostructure of the film [20] as in this paper. Similarly, the speed of adsorption determines the response/rise time and the desorption process decides the recovery time. Here, the condition 1 and condition 2 type AZO film sensor response for 29mM of H$_2$O$_2$ solute is 1.33 and 1.25 respectively. The response increases for both samples, in line with increasing rising chemical concentration. The value of response time after the addition of H$_2$O$_2$ and recovery time after the removal of it is also measured for comparison. For example the response time (T90%) for AZO films in condition 1 and condition 2 is calculated as 0.66 min and 7.56 min, respectively, for 0.29 mM of H$_2$O$_2$ solute as shown in figure 8.

![Figure 8. (a) Plot of Response (Rg/Ra)](A) (b) Rise time and (c) Fall time as function of Concentration of H$_2$O$_2$ for AZO thin film in condition 1-with vacuum and Condition 2 -without vacuum.

Similarly, the recovery time (T90%) of AZO films in condition 1 is figured as 6.3 min, whereas condition 2 based films has a recovery time last pretty long for 14.4 min in the 0.29mM H$_2$O$_2$ case. The values indicate that the rise and fall times of AZO films with nanorod structure (condition 1) is better than those of films with granular structure (condition 2). Both the sensors fabricated from AZO film exhibiting its detection limit as 0.02 mM in a broader linear range (0.02mM to 29mM). Response due to the nanorod morphology, in initial condition can be accountable due to its morphology. It has sufficiently high surface area for the chemical to react with the sensing film thereby enabling higher response. Sensor study of the proposed AZO film in response to H$_2$O$_2$ was repeated three times for each concentration. A maximum variation of about ± 5% in the sensing response was finally recorded.

3.3. Sensing mechanisms

The oxygen species which are absorbed in higher amount on the sensing film surface leads in improved oxygen ion (such as O$^-$, O$_2^-$, O$_2^{2-}$) concentrations that are adsorbed on the surface (the reaction is shown in following equation (2))

$$O_2(gas) + V_0 <--> O^- + O_2^- + O_2^{2-}(ads) + V_0 / h$$ (2)

Here, hole is denoted by 'h'. The sensing property of the developed AZO sensor is influenced by such adsorbed oxygen ions concentration due to annealing in forming gas environment. Though the samples in condition 1 and 2 have an equal amount of adsorbed oxygen %, the assumption of the nanorod structure in condition 1 enhancing the sensing property is proved by further explanation.
In the present study, the Schottky barrier model proposed for the nanoparticles (12–15 nm) of AZO thin film forms the basis of reduction mechanism due to H$_2$O$_2$ solute. The nanoparticle size 'D' of the proposed AZO structure especially (when D < 20 nm) determines the response of sensor strongly. Considering the particle size with respect to the nuclei formed at the seed layer for the nanorod growth, the sensing film response increases notably with nanoparticles size below 20 nm [21]. The thin film response for H$_2$O$_2$ has been represented in this paper on the basis, that resistance change due to the grain boundary barrier height between the nanoparticles. Considering uniform electron concentrations in core and surface of each nanoparticle, the defect distribution along its path is neglected. Let's consider two AZO particles on the contact of the film in (i) air and (ii) H$_2$O$_2$ ambient. Following this we represent a one-dimensional Schottky barrier model as shown in figure 9.

![Figure 9. Schematic drawing of Schottky barrier model and potential energy (a) in air (b) in H$_2$O$_2$ solute](image)

In the air environment, the absorbed oxygen (O−) on surface of the AZO film forms a depletion layer. As a simple phenomenon, AZO crystallites adsorb surface oxygen molecules which in turn capture the electron leading to depletion layer. A potential barrier i.e. a raise in conduction band energy between the crystallites for the electron is formed by the influence of oxygen vacancies. However, when H$_2$O$_2$ is introduced it would react with the electrons in the same way as the ionized donors.

Therefore, more number of electrons is seized in turn increases the depletion layer further. Here, sensitivity of the AZO film due to H$_2$O$_2$ increases in the potential barrier by the captured electrons. A one-dimensional model is proposed with an assumption that depletion layer width (w) is much smaller than the grain size in which q representing the electron charge, qV(x) being the potential barrier of electrons and electric potential V(x) for a given depth. Potential barriers for electrons in air coined as qV$_{bs}$ (air) and in H$_2$O$_2$ atmosphere as qV$_{bs}$ (solute). The depletion layer width (w) in both conditions which forms base for calculating the total charge density, $\rho(x)$ = $q [N_d^+(x) - n(x)]$ of the nanoparticles for the n-type AZO semiconductor. Here $N_d^+$ is ionized donors density and n is the electron density for a given depth.

Donor density $N_d$ is assumed to be uniform throughout the AZO grain considering that adsorbed oxygen in air seizes the electrons in depletion layer. Then in such a case, all donors can be considered to be ionized completely, leading to formulate an abrupt charge model for $\rho(x)$, the space charge density in air [21] as Eq. (3)

$$\rho(x) = qN_d \quad 0 < x < w \quad (3)$$

Where, $x$ denotes depletion depth from the surface, Potential distribution V(x) across the center of AZO film is represented in terms of charge carrier density $\rho(x)$ using Poisson’s equation. In air...
environment a radical change in potential barrier due to adsorbed electrons is well elucidated in figure 9(a), which indicates the $V(x)$ - the depletion region of AZO crystallites. Its corresponding equation is given by

$$V_d(x) = \frac{QN_d}{2\epsilon}(x - w)^2$$

(4)

Similarly, AZO crystallites exposed to $H_2O_2$ seizes parts of the electrons with an assumed uniform density of $n_r$. Therefore, the surface potential barrier in air, $qV_{bs}$ (air), and the surface potential barrier in $H_2O_2$ ambient, $qV_{bs}$ (solute) could be calculated as given in eq.(5) and eq.(6).

$$qV_{bs(air)} = \frac{q^2w^2N_d}{2\epsilon}$$

(5)

$$qV_{bs(solute)} = \frac{q^2w^2(N_d + n_r)}{2\epsilon}$$

(6)

In our case the potential barrier $qV_{bs}$ (solute) increases with addition of $H_2O_2$ at increasing concentration. The indication of the captured electrons by the solute reflects in the increasing resistance as shown in figure 9. The exponential relation between electrical conductivity ($\sigma$) of AZO film and barrier potential is $\sigma \propto \exp(-qV_{bs}/kT)$. $q$ is the electron charge. The inter-grain potential modification upon $H_2O_2$ is the major reason of high sensitivity from the previous reports [15,16]. The gas sensitivity increases in accordance with decreasing crystal size, adding to it, the sensitivity also relates to the metal oxide morphology. The mechanism of electrochemical reduction of $H_2O_2$ is as follows,

$$H_2O_2 + e^- \rightarrow OH_{ads} + OH^-$$

(7)

$$OH_{ads} + e^- \rightarrow OH^-$$

(8)

confirming the results in this paper matches the reported nanostructure behavior [16]. Calibration curves for the AZO film sensor were obtained by plotting the response against its concentration is shown in figure 10.

Figure 10. The calibration curve of the Response vs concentration of $H_2O_2$

The range of $H_2O_2$ levels (0.015mM to 29mM) shows a linear variation of response towards concentration. The proposed sensor showed a detection limit of 1.02 $\mu$M (S/N=3).
From table 3, we can see that the AZO nanorod thin film sensor shows high linear range, with comparably accepted LOD. The good performance of the thin film is mainly attributed by the connected nanorod structure, yields a high surface area for the sensing response; on the other hand, the structure itself is preferable for the electron transfer between nanoparticles. The reality of linear range on metal oxide sensing devices was already observed for [28] the detection of H$_2$O$_2$ and also reported here for AZO film.

**5. Conclusions**

In summary, we have fabricated a new connected nanorod thin film sensor based on AZO using solution process. The nanorod sensors exhibit higher response to H$_2$O$_2$ in room temperature. Importantly, the sensor exhibits detection limit of 1.02 μM (S/N=3) and shows high sensitivity for ethanolamine (1660%), acetic acid, (4.34x10$^6$%) with a simple but reliable fabrication process. The nanorod structured thin film built by the solution process shows excellent sensor performance and can be applied as interface layer in optoelectronic applications. The valence band characteristics of the AZO/Ag interface further illustrates and confirms that the small energy barrier plays a key role in the gas detection. As a result, all the performance illustrates the bright prospects of our new approach in the development of next-generation thin films efficient for chemical/gas detection.

**Conflicts of interest:** There are no conflicts to declare.

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**References**


### Table 3. Comparison of performances based on different ZNO based H$_2$O$_2$ sensor

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sensing material</th>
<th>Linear range µM</th>
<th>LOD* µM</th>
<th>Ref</th>
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<tbody>
<tr>
<td>1</td>
<td>Ag nanoparticles/ZnO nanorods</td>
<td>8–983</td>
<td>0.9</td>
<td>[22]</td>
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<tr>
<td>2</td>
<td>ZnO film</td>
<td>2-550</td>
<td>0.42</td>
<td>[23]</td>
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<tr>
<td>3</td>
<td>ZnO NR</td>
<td>0.25 to 10</td>
<td>0.125</td>
<td>[24]</td>
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<tr>
<td>4</td>
<td>Fork like ZnO NR</td>
<td>50 to 700</td>
<td>0.3</td>
<td>[25]</td>
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<td>5</td>
<td>Nanosized flower-like ZnO</td>
<td>10 to 1800</td>
<td>2</td>
<td>[26]</td>
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<td>6</td>
<td>Porous nanosheet-based ZnO microspheres</td>
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