Growth conditions effects on the H$_2$ and CO$_2$ gas sensing properties of Indium Tin Oxide

S. Isik$^1$, O. Coban$^1$, C. Shafai$^2$, S. Tuzemen$^1$ and E. Gur$^1$

$^1$Department of Physics, Faculty of Science, Ataturk University, Erzurum, Turkey.
$^2$Department of Electrical and Computer Engineering, University of Manitoba, Winnipeg, Canada.

E-mail: emregur@atauni.edu.tr

Abstract. Indium Tin Oxide (ITO) thin films are transparent conducting wide bandgap oxide. In this study investigated optical, structural and morphological properties of sputtered ITO thin films using X-ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDX) and optical absorption techniques. These measurements revealed that the oxygen gas percentage present in the ITO film deposited by RF magnetron sputter deposition showed systematic variation of its band gap, crystal orientation, growth rate, figure of merit (FOM) and dominant XRD peaks. All the thin films deposited at room temperature (RT). Once characterization of the films carried out, H$_2$ and CO$_2$ resistive gas sensors fabricated by depositing the ITO film on top of aluminium interdigitated contacts/electrode (IDE), that fabricated following lithography and etching processes. These devices showed reasonable sensitivity for pure H$_2$ and CO$_2$ at elevated temperature. A correlation found between the thin film properties of the ITO and its sensing capability for H$_2$ and CO$_2$, which these gases are important in many fields such as automotive, energy, biological and health-related applications.

1. Introduction

Gas sensor devices play mandatory role detecting, order less, toxic and explosive gases because of higher requirement and uses in day-to-day life from last few decades. Those gases extensively applied in industries such as transportation, industrial processes and monitoring environmental pollution and domestic safety [1]. For instance, Hydrogen (H$_2$) gas is widely used as fuel source in clean-energy transportations and power generation applications [3]. On the other hand, CO$_2$ concentrations are required in indoor spacing, agriculture field and bio-related processes [4]. Consequence to supply the demand of gas sensors powerful electrical sensing systems, high sensitivity, durable type of sensors are required to provide comprehensive detection of external physical parameters while maintaining easy of fabrication, simple operation, low production cost and miniaturization [1,2]. Especially gas sensors should design to achieve surface-to-volume ratios for better performance [5]. Recently, the indium tin oxide thin (ITO) film can be seen remarkable attention in gas sensors designing. Importantly ITO is a n-type semiconductor with a wider bandgap (3.5–4.06 eV). Furthermore ITO shows superior electrical conductivity, very high transmittance and high optical transparency. ITO also called as transparent conductive oxide (TCO) and its properties process dependent [6]. In this study resistive based simple ITO thin film sensitive layer prototype H$_2$, CO$_2$ sensor successfully fabricated and tested employing RF-magnetron sputtering the method, which characterized by high purity, low substrate temperature, good interfacial adhesion, high thickness uniformity, homogeneity qualities [7].
2. Experimental

2.1. Sample information and growth process

First Indium tin oxide (ITO) thin films between 500nm-800nm thickness deposited on soda lime glass (SLG) substrate and interdigitated electrodes (IDE) patterned SLG substrate by reactive magnetron RF sputtering technique. To realize the deposition the used target was in 14 cm diameter ITO metal with high purity (ITO - 99.99%; 90% In$_2$O$_3$ and 10% SnO$_2$), in pure Argon and Ar/O$_2$ plasma. Furthermore, surface of the ITO thin film optimized by changing O$_2$ partial pressure that has impact on crystallographic structure and opto-electrical properties of the thin films and on sputtering chamber conditions. Prior to this process typical contaminants removed from the substrate. All of experimental conditions that grown ITO thin films tabulated in Table 1. Especially, throughout the study 2”x3” soda lime glass substrate used for thin film deposition and sensor device fabrication. In the middle of the experiment, Argon and O$_2$ percentage controlled to be form ITO with respect to the sputter total pressure.

Second, all of used chemicals in this study were commercially available products applied without further processing. Prior to the deposition of the thin films, the substrates cleaned to remove particles and contaminants on the surface. These cleaning procedures conducted two different ways for substrate utilized for thin film and substrate for device design. For the first case, the substrates washed in acetone for three minutes to remove organic impurities before rinsed in isopropanol (IPA) and methanol. Later de-ionized (DI) water used to soak the substrates from the solvents. After that substrates blown dry in nitrogen (N$_2$). All sample prepared for the thin film deposition cleaned by degassing one minute and 60-minute ultrasonic bath in the DI water then rinsed with acetone, followed by cleaning IPA, DI water and drying with nitrogen gas blow off. Soon after, all samples dried on the hot plate at 110°C for the 30 minutes duration. Nitrogen blow off dry and IPA solution used for clean sample holders tools and chucks whenever required. Then to second case that substrate used for device fabrication thoroughly cleansed by immersing in piranha solutions (H$_2$SO$_4$ - 98% and H$_2$O$_2$ -30% 4:1) in volume after following with ultrasonic cleansing for 10 min. Initially the substrates washed in acetone for three minutes to isopropanol alcohol and deionized (DI) water then dried using dry nitrogen flow. Cleaning process removed surface particles, any impurities organic contaminants, and native oxides and substrate converted to surfaces to be hydrophilic.

Third, in this study three types of patterns and three different sizes (¼ mm, ½ mm, and 1mm) selected to design for image of gas sensor device. Our focus was to give geometrically good surface volume ratio for the sensor device to enhance resistance. Later using computer aid L-edit standard CAD tool supported software from Taner EDA© designed the photo mask. A photo mask is a piece of glass that uses to transfer the design to a material layer that wish to pattern for processing. The physical properties of each mask fabricated using 5” x 5” soda lime glass 0.09” thick Chrome coated (approx. 70nm thick). Further the polarity of mask decided (Inverted polygons=chrome vs. Non-Inverted polygons=glass) for go along with 504 positive PR. As a next step, aluminum coated substrate is held on a spinner chuck by vacuum and resist is coated to uniform thickness by spin coating (3000-6000 rpm for 15-30 seconds). Typically 80-100, p=resist solids content in percent w=spinner rotational speed in rpm/1000. To proceed lithography 500nm Al sputtered thin film 2”x3” glass substrate moisturized by DI water. Soft baker tested for SLG surface temperature before bake state for SLG as it designed for Si substrate. Soft Baker adjusted temperature 110°C for 2 minutes for the glass substrate and because of Al cooling very fast. Reasonable amount of 504 PR spread over Al deposited glass substrate by the spine coating. Resist 50/50 500 RAMO for 10 seconds, Spread 100 for 10 seconds and spine 300 for 30 seconds. The thickness measured of Al thin film after deposition that varied from 200nm to 900nm. More over photo resist thickness varied from 1.700µm to 3.1 µm. Later prebake (soft bake) used to evaporate the coating solvent and to densify the resist after spin coating. Consequent a narrow time-temperature window needed to achieve proper line width control. Further 504 PR coated sample glass kept under 210°C in soft bake hot plate for 2 minutes. The glass moisture by DI water and dried by N$_2$ gas blow. Then 504 PR coated glass kept on mask aligner holder and...
mounted the photo mask top of the glass holder then exposed 5 seconds for UV light. Once done that, developer arranged to the 10-second pre wet, 20 second develop, 10 seconds dwell, 20-second rinse and 20-second spine. Usually post bake used to stabilize and harden the developed photoresist prior to processing steps that will resist transferred pattern. Later the lithographed glass kept in hard baker (post bake) at least for 30 minutes at 110°C after we confirmed the patterns transfer in to the glass as expected. In this process, etch back method followed to etch unwanted Al film. So Al thin film cleaned out UV exposed areas of the glass substrate using the Al etch solution which heated 70°C, 138 Rpm rotating and on the 134 heated hot plate for two (2) minutes in the acid wet deck cleansed by DI water immediately and followed drying by N₂ gas. After etching, the Al of the well-dried glass substrate removed the PR by acetone in lithography wet-deck.

Table 1. Chamber Set up Conditions for ITO.

| Parameter     | Value                   |
|---------------|-------------------------|
| P\text{Base}  | 2.8 \times 10^{-6} Torr |
| P\text{Total} | 9.7 \times 10^{-3} to 9.9 \times 10^{-3} Torr |
| Power         | 300W                    |
| Target (d)    | 14 cm                   |
| Offset        | Ar – 2.1, O₂ - 1.7      |
| Time          | 15 minutes for all Samples |

Table 2. Bandgap variation with P(O₂) %.

| P(O₂) % | Bandgap |
|---------|---------|
| 2.7     | 3.68    |
| 6.9     | 3.79    |
| 25.0    | 4.13    |

Figure 1. (a) Lithography process for ITO gas sensors; (b) Schematic drawing ITO deposited thin film device & cross sectional view; (c) Physical ITO deposited device under microscope.
2.2. **ITO thin film sensor measurements**

All gas sensitivity measurements and performance evaluation of flexible Hydrogen and CO\textsubscript{2} Sensors carried out by a noncommercial available prototype gas measuring system (Figure 2). Before taking sensor measurement, the sensor Interdigitated Electrode/Contacts (IDE) tested for ohmic behavior at room temperature (RT), elevated temperatures, and then confirmed by I-V measurements. Once obtain expected ohmic behavior gas sensing evaluation performed by allowing inert and target gases into the chamber in alternative manner, and the target gas content adjusted by MFC inlet flow rate of 400 sccm. During the experiment, the substrate temperature was 200 °C, external bias voltage was 1.0 V supplied by a Keithley 487 picoammeter/voltage source. Each Hydrogen and CO\textsubscript{2} sensor fixed in a sealed chamber that flowed with hydrogen gas, CO\textsubscript{2} gas or Argon. The two probing electrodes of each sensor were mounted on a standard probe holder on an Al heater plate and connected to a computer controlled Keithley 487 which integrated by LabVIEW program. All measurements carried out at RT and elevated temperatures (30 °C - 200 °C).

![Figure 2](image.png)

**Figure 2.** (a) Real time gas measurement system; (b) Schematic drawing of the gas delivery system.

Sensitivity, response time and recover time analysis and measurement calculation of gas sensors carried out according to method in the Figure 6. Response was determined using \( R = R_{air}/R_{gas} \) and response time and recovery time of the sensors defined as the time taken for the resistance to change by 90% on exposure to the target gas and Ar respectively. The response and recovery times defined as the time required for a change of the resistance to reach 90% of the equilibrium value after injecting and that for removing the detected gas, respectively by inlet and outlet. When air in standard cubic centimeter per minute (sccm) flow level target gas were flowed through the sensor element, the corresponding steady state resistances of the sensor in air (\( R_{air} \)) and in the air + gas target (\( R_{gas} \)) were recorded, respectively. Thus the sensor response (S) for oxidizing gas for instance CO is defined as the ratio of \( R_{gas}/R_{air} \), while the response for reducing gas (H\textsubscript{2}) is defined as the ratio of \( R_{air}/R_{gas} \). In all cases, flow of Ar (99.999%) and H\textsubscript{2} (99.9999%) was used to fill the chamber and the H\textsubscript{2} concentration was controlled using gas flow. Initial stabilization, prior to the measurements, was obtained by flowing 100% H\textsubscript{2} until the electrical current at a constant voltage became stable.

2.3. **ITO thin film Analysis (XRD, SEM, EDAX and Absorption Techniques)**

The surface morphology of the ITO thin films grown by sputtering in this study was observed by SEM (Scanning Electronic Microscope - QUANTA 450 FEG:FEI Company branded) and data of XRD (X-Ray Diffraction) were taken in a computer controlled diffractometer and with X-ray generator Cu K\textsubscript{α} radiation from an X-ray tube with normal focus X-ray diffraction (PANALYTICAL/Empyrean...
branded XRD). Furthermore optical absorption/transmission measurements of the films measured in UV-visible-near infrared region by using a Perkin Elmer UV-VIS 2 Lambda spectrometer, which is available for wavelengths in the range of 200 nm to 1100.

3. Results and Discussion

3.1. XRD, SEM, EDAX and Absorption Analysis
First, the Figure 3 (c) shows SEM image of RF sputtered ITO thin films deposited in Ar/O2 plasma chamber that exhibit nano-sized grains. All those ITO thin film deposited in O2 plasma chamber given rod like and more compact square shape grains. Examination and comparisons of these images clearly reveals that significant surface morphology induced by depositing with and without oxygen of ITO thin film resulted by sputtering technique.

Second in order to investigate behavior observed in the ITO sensor, we performed XRD analyses. The Figure 3 (a) shows that crystal formation of ITO thin film surface significantly affected by plasma chamber. The peak positions and full-width-at-half-maximum (FWHM) values of the diffraction peaks influenced ITO confirms increasing oxygen partial pressure and dominant peak found to be (400). Furthermore, the XRD results show the thin films generally poly crystals & multiple peaks. More over EDAX results confirmed the thin film composition for comparison the outcome.

Third Figure 4 (a) shows absorption measurements of ITO thin films grown at rich O2 partial pressure that the causes to shift in the absorption spectrum of the ITO thin films. Absorption measurements plotted reference to the SLG substrate. Hence, the absorption spectrum of the SLG glass sample has shown to confirm the observed absorptions due to the grown thin films. Therefore plots that shift in the absorption spectrum in the range of 250 nm while the ITO films show the absorption spectra increase between 350-400 nm. More over the transmittance values are above 90% that gives lowest possible electrical resistivity with the optimized highest transparency helps sensitivity (FOM) of ITO thin film according to the values of Table 3. FOM also calculated and included in Table 3, which gave higher results that suitable for TCO gas sensors.

Furthermore, we calculated bandgap with respect to O2 partial pressure that increases O2 given in plasma chamber. Figure 4(c) shows the absorption coefficient versus incoming light energy variation of the samples and the calculations of the bandgap from the square of the absorption coefficient. Figure 4(c) absorption coefficient and 4(d) Square of absorption coefficient vs energy graph for ITO (2.7% O2) shows the fit to find the bandgap value of the thin film. Figure 4 (d) graph shows red line - fit made on the plot to calculate bandgap. The band gap for pure ITO 2.7% O2 was Eg=3.68 eV obtained as in Table 2.

![Figure 3](image)

*Figure 3.(a) XRD; (b) EDAX image & Composition analysis; (c) SEM image for P (O2)=2.7%*
Figure 4. (a) Absorption measurements of the ITO thin films (200-450 nm); (b) high transmittance; (c) Absorption coefficient; (d) Square absorption coefficient vs energy graph for bandgap calculation ($P(O_2) = 2.7\%$).

Table 3. Effect of FOM with $P(O_2)\%$.

| $P(O_2)\%$ | Transparency | FOM         |
|------------|--------------|-------------|
| 2.7        | 0.92         | $0.37 \times 10^{-5}$ |

3.2. Gas sensor measurements analysis
The results obtained from gas sensor measurements system tabulated in Table 4 and Table 5 for ITO 3 device that contain 16.3\% oxygen in the plasma chamber while depositing thin film. Reducing $H_2$ and $CO_2$ gases sensitivity observed by resistance versus time graph by integrated LabVIEW program in real time showed resistance changes. Nevertheless, adsorption mechanism of $CO_2$ different from reducing gas $H_2$, both type of sensors displayed better sensitivity and obeyed step response of first order sensor response. Hydrogen sensor showed highest sensitivity, response time and recovery time according to the calculations. Consequence $CO_2$ also showed similar sensitivity, response time and recovery time values for ITO 3 sensor device.
Figure 5. ITO 3 (16.3% O₂) Device at 200ºC; (a) H₂; (b) CO₂.

Table 4. Responsivity, Response Time, Recovery time for H₂ at 200 ºC.

| Responsivity ((R₁-R₀)/R₀)*100 | Response time(s) (1-1/e) | Recovery time(s) (1/e) |
|--------------------------------|--------------------------|------------------------|
| 10.9                          | 32.8                     | 36.4                   |

Table 5. Responsivity, Response Time, Recovery time for CO₂ at 200 ºC.

| Responsivity ((R₁-R₀)/R₀)*100 | Response time(s) (1-1/e) | Recovery time(s) (1/e) |
|--------------------------------|--------------------------|------------------------|
| 9.2                            | 38.9                     | 62.1                   |

Figure 6. Calculating response time and recovery time.
4. Conclusions
The ITO (TCO) thin films prepared by RF magnetron sputtering technique are good gas sensing materials. It has showed reasonable sensitivity to reducing H\textsubscript{2} and CO\textsubscript{2} gases. The sensitivity of ITO thin films was remarkably affected by O\textsubscript{2} content introduced to growth plasma chamber. The optimal working temperature to detect H\textsubscript{2} and CO\textsubscript{2} was 200 \degree C. From the obtained results, the ITO thin film sensors shows potential for gas sensor application and further investigations are necessary to develop high performance gas sensors.

5. Acknowledgements
This work gas measurement system was financially supported by Atatürk university Bap project number 2015/93 which is gratefully acknowledged.

References
[1] Nakamura Zhang J, Liu X, Neri G, and Pinna N 2015 Nanostructured Materials for Room-Temperature Gas Sensors Adv. Mater. 2015, DOI: 10.1002/adma.201503825 (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)
[2] Huang L, Zhang Z, Li Z, Chen B, Ma X, Dong L, and Peng L Multifunctional Graphene Sensors for Magnetic and Hydrogen Detection ACS Appl. Mater. Interfaces 2015, 7, 9581−9588 DOI: 10.1021/acsami.5b01070
[3] Shin D H, Lee J S, Jun J, An J H, Kim S G, Cho K H and Jang J Flower-like Palladium Nanoclusters Decorated Graphene Electrodes for Ultrasensitive and Flexible Hydrogen Gas Sensing Scientific Reports 2015 5:12294 DOI: 10.1038/srep12294
[4] Kenji Obata a, Shizuko Kumazawa b, Shigenori Matsushima a, Kengo Shimanoe c, Noboru Yamazoe c NASICON-based potentiometric CO\textsubscript{2} sensor combined with new materials operative at room temperature Sensors and Actuators B 108 (2005) 352–358
[5] S. Xu, Y. Shi Low temperature high sensor response nano gas sensor using ITO nanofibers Sensors and Actuators B 143 (2009) 71–75
[6] C.W. Lin et al. On an indium–tin-oxide thin film based ammonia gas sensor Sensors and Actuators B 160 (2011) 1481–1484
[7] H.S. Al-Salman, M.J. Abdullah Hydrogen gas sensing based on ZnO nanostructure prepared by RF-sputtering on quartz and PET substrates Sensors and Actuators B 181 (2013) 259–266