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# ITO gas sensors for $CO_2$ and $H_2$ detection

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## Abstract

Thin films with extensive characteristics and surface morphology are very important in designing high performance and reliable gas sensors. Therefore, comprehensive study carried out on ITO transparent conductive oxide resistive based H2 and CO2 gas sensors. As a result, bottom up prototype gas sensor device fabricated and tested in order to understand those properties and behaviors that effects on sensitivity. All the thin film deposited employing RF magnetron sputtering technique investigated by SEM, XRD, EDAX and Absorption methods. Different oxygen partial pressure introduced as a variable to optimize the surface thin film. Those synthesized material properties showed reasonable correlation with the sensitivities and response of ITO devices for reducing H2 and CO2 gases.

**Key Words:** Gas sensors, CO2 sensor, H2 sensor, RF sputtering, ITO

# CCD ve CMOS Sensörlerin Çalışma Prensipleri ve Astronomi Alanındaki Yeri

## Özet

Yüksek perfromanslı güvenilir gaz sensörlerinde ince filmlerin detaylı karakteritikle ve yüzey morfolojileri çok önemlidir. Bu nedenle şeffaf iletken oksit İTO direnç tabanlı H2 ve CO2 gaz sensörleri üzerinde kapsamlı bir çalışma yapılmıştır. Sonuç olarak, hassasiyete etki eden özellikleri ve davranışları anlamak için aşağıdan yukarıya prototip gaz sensör cihazı üretilmiş ve test edilmiştir. RF magnetron püskürtme tekniği kullanılarak biriktirilen tüm ince filmler SEM, XRD, EDAX ve Soğurma yöntemleri ile incelenmiştir. İnce filmlerin yüzey yapılarını optimize etmek için, değişken oksijen kısmi basıncı altında filmler büyütülmüştür. Sentezlenen bu malzemelerin özellikleri, H2 ve CO2 gazlarını indirgemek için ITO tabalı gaz sensörü aygıtlarının duyarlılıkları ve tepkisi ile kabul edilebilir bir korelasyon gösterdi.

**Anahtar Kelimeler:** gaz sensör, H2 sensör, ITO

## 1. Introduction

The gas sensors are requisite devices in regular life for detection odorless, hazards, toxic or explosive gases concerning public safety and environmental protection. Consequence of variety of technology and materials has been experimented to invent and explore best suited qualities of materials for improving characteristics of the sensors such as sensitivity, selectivity, and calibration stability, temperature [1,2]. Among those electronic noses, H2 and CO2 sensors started to flourish for their importance in variety of industries, transportation, environmental and health related fields. For instance, high pressure hydrogen gas becoming one of the most important alternative energy known as green energy with zero emission [1]. Thus hydrogen leak detection sensor technology became one of the priority concerns about reliability, safety, and economic reasons [2]. On the other hand, measurement and regulation of CO2 gas is required in indoor spacing, agriculture field and bio-related processes [3]. Even though number of H2 and CO2 sensor exist, those are not sufficient when considering demand, simplicity and the cost perspective.

The indium tin oxide (ITO) wide optical band gap semiconductor thin films as a sensitive layer for gas detection investigated which widely applied as transparent conducting electrodes in flat-panel displays (FPD) [4], solar cells [5], and organic light emitting diodes (OLEDs) [6] due to their process dependency and highly degenerate electrical conductivity [8], high optical transparency [7]. ITO also can be considered as doped from In2O3 materials, known that very common material for gas detection[8]. Furthermore, ITO thin films with careful control of synthesis conditions can be achieved relatively low resistivity while maintaining high transparency that enhance the sensitivity of gas sensors.

Various growth conditions have an effect of increment in the carrier concentrations contributing to the widening of the bandgap, which is known as the Burstein– Moss shift. In addition to the carrier concentration, growth conditions strongly affect the crystallinity, impurity levels and surface roughness of the grown films. In this work, ITO thin film deposited employing RF-magnetron sputtering on soda lime glass substrate that method which characterized by high purity, low substrate temperature, good interfacial adhesion, high thickness uniformity and homogeneity [9]. The effect of O2 partial pressure, on the structural, optical, and sensing properties of the ITO thin film deposited by RF-magnetron sputtering were successfully investigated. Furthermore, resistive based simple concept, low cost, repeatable, mass scale gas sensor device based on ITO thin film sensitive layer gas sensors fabricated. All thin film deposited on interdigitated electrodes (IDE) soda lime glass substrate operated at room temperature without post heat treatment. Moreover, structural and surface characterizations carried out by absorption techniques, x-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). With help of analysis techniques remarkable transmittance and figure of merit observed. Importantly mechanism analysis were undertaken to study the correlation between the sensor performance and the materials structure. The gas-sensing properties of the thin films were examined exposing the H2 and CO2 gas. The relationships between O2 content and sensor performances were concluded. The influencing characteristics in the evaluation of the thin film also discussed. The gas sensitivity is explained by a change of the band bending on the surface of the metal oxides caused by adsorption of gas molecules. It is expected and proved that these prepared ITO thin films are promising for a H2 and CO2 gases.

## 2. Experiment

As illustrated in Figure 1, CO2 and H2 ITO sensors were fabricated through microfabrication process based on radio frequency (RF) magnetron sputtering system derived from 14 cm ITO metal target with high purity (ITO - 99.99%, 90% In2O3 and 10% SnO2), in pure Ar and Ar/O2 plasma. Indium tin oxide (ITO) thin films with a thickness of between 500nm-800nm deposited on soda lime glass (SLG) substrate and IDE patterned SLG substrate by reactive magnetron RF sputtering technique. The deposition optimized by changing O2 partial pressure that has impact on crystallographic structure and opto-electrical properties of the films and on sputtering chamber conditions. The partial pressure of the oxygen in the chamber was varied up to 25% of growth pressures.

Standard cleaning procedure (ultrasonic bath of acetone, isopropyl, methanol and de-ionized water for 5 min.) followed to remove contaminants prior to deposition of ITO thin film and samples used in the device. The sensor fabrication was subjected to series of lithography process to fabricate all prototype sensors. As seen in the right side of the Figure 1, the lithography process was started with the photo resist coating by spin coating system under 5000 rpm condition for 50s followed by a soft bake at 110 0C. After exposure of UV light with the mask aligner SUSS Microtech MJB4, developing step was done for 5 min. The lithography process was finished by the hard bake at 120 0C for 2 min. All the sensors sensitivity measurement obtained by non-commercially available gas measuring system.

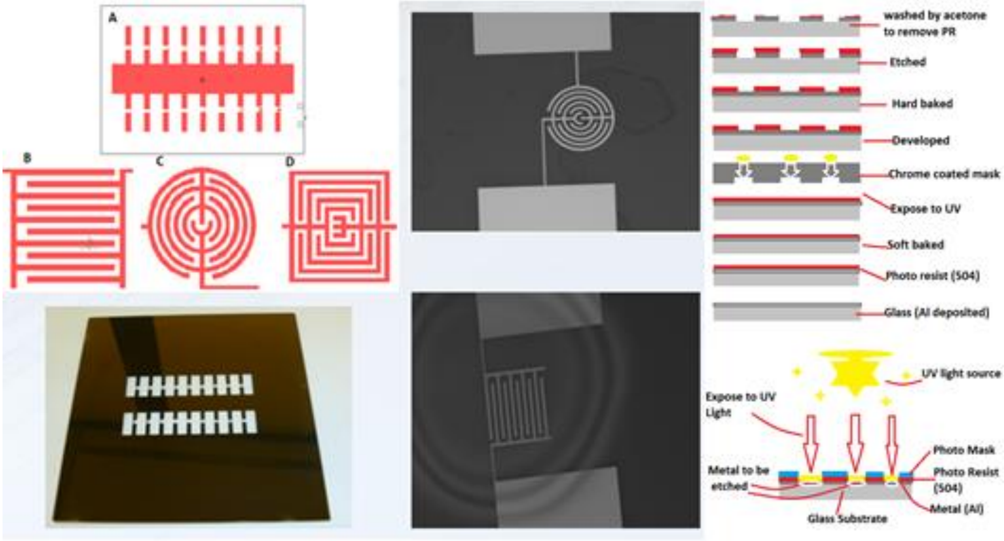
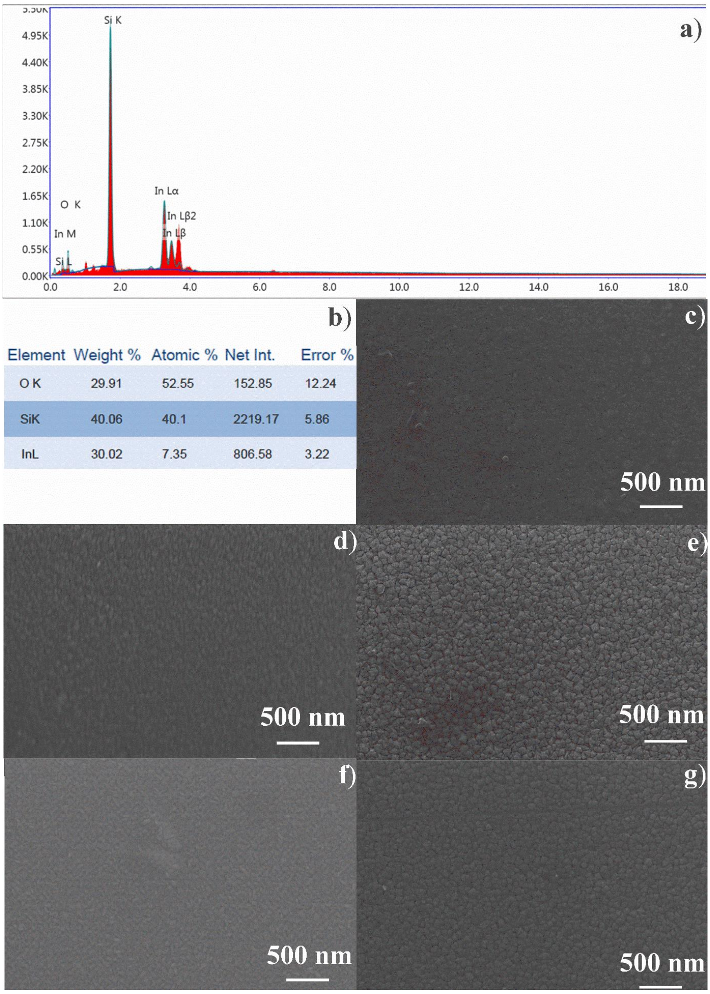


**Figure 1.** ITO thin film growth and sensor fabrication process.

The morphology characterization of the samples grown was performed with (FESEM) with Zeiss Sigma 300. The elemental analysis also was conducted with energy dispersive x-ray (EDX) detector attached to the FESEM system. The XRD measurements were made θ-2θ condition between 10-90-degree PANalytical Empyrean XRD system.

## 3. Results and Discussion

From EDX composition analysis in Figure 2 a and the results in tabulated in Figure 2 b show that ITO film grown with ITO target deposited with pure Ar plasma with no oxygen gas contain zero Sn. This could be the result of that indium was formally evaporated because of its lower boiling point than Sn [10]. On the other hand, as the oxygen is included during the growth, the Sn composition appears in the EDX measurements (figures not shown). The Sn amount in ITO thin film is an important factor to



| Element | Weight % | Atomic % | Net Int. | Error % |
|---|---|---|---|---|
| O K | 29.91 | 52.55 | 152.85 | 12.24 |
| SiK | 40.06 | 40.1 | 2219.17 | 5.86 |
| InL | 30.02 | 7.35 | 806.58 | 3.22 |

**Figure 2.** a) EDX data for the ITO grown under no oxygen pressure b) EDX element analysis c)-g) FESEM images of the ITO films of different oxygen partial pressure percentages to the total growth pressure 0%, 2.7%, 11.7%, 13.5%, 16.3%, respectively.

decrease the resistance of prepared ITO film [11], this no Sn contain sensor has shown the highest sensitivity. Figure 2 c-g have shown the FESEM images of the ITO thin films grown under different oxygen partial pressure percentages, 0%, 2.7%, 11.7%, 13.5%, 16.3%, respectively. It is shown that as the oxygen partial pressure percentage increases, the grain sizes observed in the FESEM images increase which is maximum for the 11.7% grown ITO film.

Figure 3 shows the XRD pattern of the sputtered ITO grains. The dominant peaks are indexed as (400) and (441) crystal faces of ITO which confirmed that the gains are polycrystalline. Increasing with the O2 content, the peak intensities belong to the ITO planes are increased as seen in the figure. Table 1 shows the calculated D values from the measured of the XRD data. The D values varies between 27 nm- 77 nm as seen in the table.

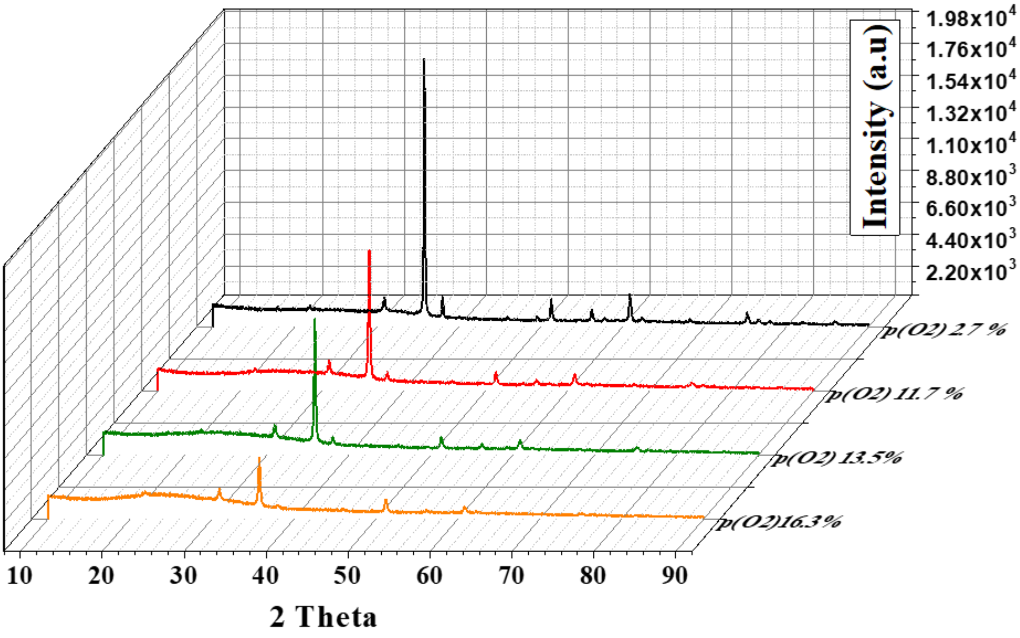


**Figure 3.** XRD figure of ITO films grown different O2 partial pressures

**Table 1.** Detail analysis of the XRD measurements

| $O_2$% | Thickness (nm) | 2θ (400) | I% (400) | FWHM (400) | D (nm) | 2θ (441) | I% (441) | FWHM (441) |
|---|---|---|---|---|---|---|---|---|
| 0 | 333 | - | - | - | - | - | - | - |
| 2.7 | 983 | 35.8 | 100 | 0.13 | 62.8 | 51.3 | 8.61 | 0.17 |
| 11.7 | 250 | 35.8 | 100 | 0.30 | 27.8 | 51.2 | 82.6 | 0.20 |
| 13.5 | 335 | 35.8 | 83.9 | 0.19 | 56.5 | 51.2 | 100 | 0.16 |
| 16.3 | 825 | 35.7 | 100 | 0.11 | 76.6 | 51.1 | 15.6 | 0.17 |
| 25 | 402 | 35.8 | 100 | 0.21 | 39.4 | 51.2 | 29.4 | 0.23 |

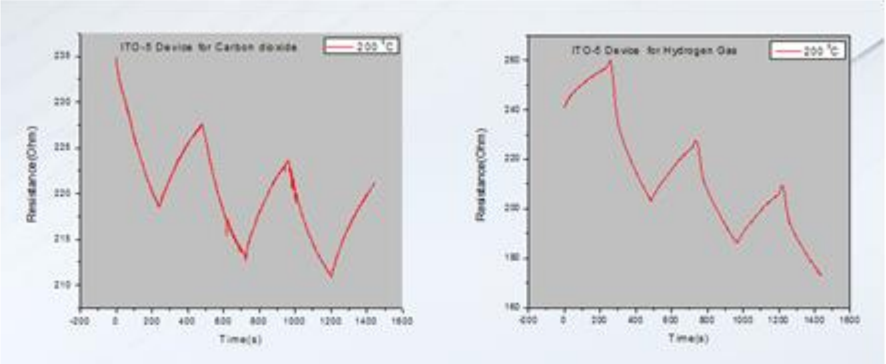


**Figure 4.** CO2 and H2 responses of the ITO sensor grown under 0% oxygen pressure.

Figure 4 shows a representative dynamic curve of the ITO sensor grown with no oxygen gas in the chamber. The concentration of $CO_2$ and $H_2$ for this test was 400 sccm. The optimal temperature to detect $CO_2$ and $H_2$ gases is at 200 $^0$C which is plotted in Figure 4. The optimal working temperature is relatively lower than that of ITO thin film sensor which reported in other studies [7]. The resistance change, $\Delta R$, of the sensors is monitored during sequential or periodic exposures to $H_2$ or $CO_2$. $\Delta R/R_0$ (sensitivity) is defined as the percent resistance change upon exposure to a gas with a fixed concentration of hydrogen and is calculated according to $\Delta R/R_0 = (R - R_0)/R_0$ where $R_0$ is the resistance of the sensor exposed to $N_2$ air and R is the maximum resistance after exposure to a gas containing hydrogen. Consequently, decreasing of the work function is beneficial to the flow of more electrons, resulted in decreasing of the resistance [12].

Good sensitivity (22%) of ITO sensor that contains no oxygen flow included during the growth could be related to the surface to volume ratio of nano-grains of the thin film. Table 2 and 3 have shown the responsivity, response and recovery time for some of the ITO sensors produced in the study. Recovery times for the $CO_2$ sensors are long. The reason for longer recovery time might be attributed that it took longer time for $CO_2$ desorbing from the nano-gains. A detail investigation expecting to carry out in future studies to find $CO_2$ adsorbing and desorbing by thin film. The fact that ITO nano grains have very large surface to-volume ratio which means a significant fraction of the atoms of ITO are surface atoms that can participate in surface reactions. This feature would contribute the resistance change of the ITO nano-grains, thus enhance the response the sensor and optimal working temperature. Another reason was related to the nature of the ITO surface, which was easy to react with $H_2$ because Sn doped material reported good sensitivity for $H_2$. Table 2 and Table 3 have shown the performances of the gas sensors characteristics.

**Table 2.** Responsivity, Response Time, Recovery time for $H_2$ at 200 $^0C$

| Responsivity<br>((R-R$_0$)/R$_0$)*100 | | | Response Time(S)<br>(1-1/e) | | | Recovery time(s)<br>(1/e) | | |
|---|---|---|---|---|---|---|---|---|
| 2.7% | 25% | %0 | 2.7% | 25% | %0 | 2.7% | 25% | %0 |
| 10.9 | 9.8 | 22 | 32.8 | 23.6 | 92.3 | 36.4 | 4.4 | 24.2 |

**Table 3.** Responsivity, Response Time, Recovery time for $CO_2$ at 200 $^0C$

| Responsivity<br>((R-R$_0$)/R$_0$)*100 | | | Response Time(S)<br>(1-1/e) | | | Recovery time(s)<br>(1/e) | | |
|---|---|---|---|---|---|---|---|---|
| 2.7% | 25% | %0 | 2.7% | 25% | %0 | 2.7% | 25% | %0 |
| 9.2 | 6.0 | 4.1 | 39.8 | 10.5 | 68.1 | 62.1 | 28.7 | 105.8 |

Semiconductor gas sensors are based on the conductivity changes of the semiconductor materials upon interaction with the target gas molecules. When the $H_2$ molecules were absorbed on the surface of the ITO nano-grains, electron transfer occurs between ITO and target gases. When the temperature was increased, the molecules were easier to react and be absorbed on the adsorption sties. However, desorption process existed at the same time. When the temperature was too high, the desorption process would become dominating which lowered the absorption of the gas. Consequently, there was an optimum working temperature for ITO nano-grain based sensor. A systematic investigation needed to prove further for $CO_2$. Besides the sensor response other parameters such as selectivity, response time and stability, are also very important. The testing for these parameters is in progress [13].

The dependence of the resistivity on the oxygen partial pressure is a well-known experimental result and is explained on the basis of oxygen deficiency in the film (each oxygen vacancy gives rise to two conduction electrons). Increasing oxygen content of the films by increasing the partial pressure of oxygen during the growth the samples in air or oxygen should decrease the oxygen vacancies leading to less conductive films. However, a minimum in the resistivity of the ITO thin films deposited on glass substrates is reported between 15 and 20% of oxygen partial pressure by a few investigators indicating an improvement in the crystallinity of the films (mobility of the carriers is dependent on crystallinity) [14].

## 4. Conclusion

ITO thin film has been successfully prepared by RF sputtering technique with the goals of improving sensitivity, simplicity and with RT temperature and without post heat treatment by enhancing performance of thin film controlling $O_2$ ratio for in $H_2$ and $CO_2$ sensing. The innovative sensing platforms demonstrated excellent sensitivity, response and recovery time. Device dependent sensitivities tested for range of operating temperature between of 30 °C – 200 °C. The distinct surface morphology and properties of ITO thin film with grain sizes play a key role improving sensitivity of these sensors. The present result evidently proves that the methodology that applied to design ITO sensors could be one of the most promising TCO oxide-based gas sensors.

## 5. Acknowledgment

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## Conflicts of interest

The authors declare that there are no potential conflicts of interest relevant to this article.

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