SECTION A

CHAPTER VI

\textit{In}_2\text{O}_3 \text{ Thin film coating on surface modified substrates}
6.1. Introduction

This chapter deals with the method employed to enhance the surface area of the film by using modified substrates that had been coated using method-I (discussed in the section 2.2.2.). The substrates used for the coating are Si-SiO₂ and surface modified glass. The surface areas of the glass substrates were enhanced by preparing breath figure pattern over the surface of the substrates using a polymer and evaporating it after coating the In₂O₃ solution.

6.2. Thin film coating on Si-SiO₂ substrates

P-type Si substrates were cleaned using the procedure discussed in section 4.4. The cleaned substrates were thermally oxidized in a horizontal tube furnace to form an insulating film of silicon dioxide (SiO₂) of 800 nm thickness over its surface. The oxidized substrates were then dip coated with the coating solution prepared by the method given in section 3.2.2. The coated film was annealed at 400°C for 1 hr in a box type muffle furnace. The n-type In₂O₃ thin film was coated over the insulating SiO₂ formed on the p-type Si substrate. A uniform area of 1 cm x 1 cm of the film has been taken and it has been constructed as a field effect transistor by evaporating aluminium (Al) metal over the synthesized thin film for the source and drain contacts. Thickness of the Al over the film was 250 nm and the dimension was 0.4 cm x 0.2 cm (length X breadth). Si substrate itself acts as the gate and for making contact 0.4 cm x 0.4 cm Al has been coated with the same thickness.

6.3. Results and discussion

6.3.1. Structural Analysis

Fig. 6.1 shows the XRD pattern of the film dip coated on silicon dioxide layer over a silicon wafer. The diffraction peaks in the pattern correspond to the (211), (222), (400), (411), (332), (431), (440), (611), (622), (631) and (444) planes, which can be indexed to the body-centered cubic structure for In₂O₃ (space group Ia3,
JCPDS # 06-0416). The average crystallite size (D) calculated from the full width at half maximum (β) (FWHM) using the Scherrer formula is found to be 25 nm. The lattice parameter is found to be 10.11 Å which is in close agreement with the standard body centered cubic structure of In₂O₃ (JCPDS # 06-0416). The amount of strain present in the film is found to be $1.8125 \times 10^{-3}$ lin⁻² m⁻⁴ and the dislocation density of the film is calculated as $1.6 \times 10^{15}$ lin/m².

**Fig. 6.1 XRD pattern of the In₂O₃ thin film coated on Si-SiO₂ substrate**

### 6.3.2. Surface Morphological Analysis

Fig. 6.2(a) shows the Scanning Electron Microscopic (SEM) image of the dip coated In₂O₃ thin film. Porous surface has been observed with pore sizes ranging from nano to micrometers. The same coating solution while coated on bare glass substrates does not show any porous structure. This may be due to the amorphous nature of the glass substrates. In the mean while, small spherical grains were observed through the SEM and AFM images of the films coated on bare glass substrates. Due to the orientation of the Si-SiO₂ substrate, the spherical grains were orderly formed and lead to a porous structure as depicted in the Fig. 6.3.

Surface porosity is one of the factors which enhance the surface area of the prepared thin film, which offers a number of adhesion sites to the gas molecules. The
cross sectional image in Fig. 6.2(b) shows the curved edge pores present in the film and the thickness of the porous film is found to be 375 nm. Fig. 6.4 shows the 2-D and 3-D Atomic force microscopic (AFM) images of the dip coated In$_2$O$_3$ thin film coated on Si-SiO$_2$ substrate. Spherical grains are observed in the 2-D AFM image as shown in Fig. 6.4 (a). Fig. 6.4(b) shows the 3-D image of the dip coated In$_2$O$_3$ thin film. The average roughness is found to be 17 nm and RMS roughness of the film is calculated as 24 nm.

6.3.3. FET Characteristics

A field effect transistor has been constructed using the nano-porous In$_2$O$_3$ thin film and the current-voltage characteristics of the transistor were analyzed. The carrier concentration in the film is directly related to its conductance which in turn can be altered by applying the gate voltage or by the adsorbed ethanol vapours due to its electron accepting capability [1]. The back-gate effect of the In$_2$O$_3$ porous thin film can be confirmed from the source-drain current ($I_D$) – source-drain voltage ($V_{ds}$) curves of the transistor which is shown in the Fig. 6.5. A nearly linear variation has been observed for the positive gate voltage ($V_g$), which shows the formation of a nearly ohmic contact between the film and the electrode. This behavior also contributes to the improvement of sensitivity in the gas sensor [1]. In the present work, the change in $I_D$ with respect to the change in $V_{ds}$ at constant $V_g$ has been measured, which is in turn related to the resistance of the material. The current – voltage curves have been plotted by varying $V_g$ from -300 mV to +300 mV in steps of 150 mV. The transistor is sensitive to electrostatic gating as clearly seen in the inset of Fig. 6.6 where a change of $\sim$ 380% in conductance was observed when $V_g$ was swept from 0 to 300mV. Therefore, the transistor sensor is supposed to be very sensitive to dilute molecules [1].

A similar work has been reported by Zheng et al in the construction of In$_2$O$_3$ nanowire transistor for the detection of H$_2$S at room temperature [1]. They have reported a change of up to 300% in $I_D$ for the change in $V_g$. Zhang et al reported a change of up to 40% for the detection of NO$_2$ at ppb levels [2]. In the present work, the observed change for $V_g$ in milli-voltage level is considerably more and therefore the constructed transistor sensor will be sensitive to even a dilute concentration of the gas molecules.
Fig. 6.2(a) SEM image of the In$_2$O$_3$ thin film coated on Si-SiO$_2$ substrate and 
(b) Cross sectional SEM image of the In$_2$O$_3$ thin film.

Fig. 6.3. Formation of In$_2$O$_3$ spherical grains over the ordered and unordered substrates
Fig. 6.4(a) 2D and (b) 3D image of the AFM image of In$_2$O$_3$ Coated on Si/SiO$_2$ substrate
6.3.4. Transistor Sensor

The current-voltage ($I_d$-$V_{ds}$) characteristic of the transistor sensor at room temperature was measured when $V_g$ was maintained at 0 mV. Different concentrations of ethanol vapours (5 ppm, 10 ppm, 50 ppm and 100 ppm) have been exposed to the sensor for ~ 6 min. The observed changes are shown in Fig. 6.6. Here also, a nearly linear variation was observed as in Fig. 6.5. As the concentration of ethanol increases the sensor current has also increased. When the gate voltage was varied from $V_g = 0$ mV to 150 and 300 mV, a considerable increase in the response ($I_d$) to ethanol vapours has been observed. Fig. 6.7 shows the current-voltage curves for 100 ppm of ethanol with the increase in gate voltage. The current $I_d$ is observed to increase from 260 \( \mu \)A to 315 \( \mu \)A for the change of $V_g$ from 0 mV to 300 mV.

![Current-Voltage characteristics (I_d-V_{ds}) curves of the transistor at different gate voltages. Inset shows the corresponding I_{ds}-V_g curve at V_{ds} of 10V.](image)

Fig. 6.5. Current-Voltage characteristics ($I_d$-$V_{ds}$) curves of the transistor at different gate voltages. Inset shows the corresponding $I_{ds}$-$V_g$ curve at $V_{ds}$ of 10V.
Fig. 6.6. Current-Voltage curves of the sensor recorded after the exposure of ethanol vapours at room temperature when the gate voltage $V_g$ was maintained at 0 mV.

Apart from ethanol, the sensitivity of the sensor towards ammonia and acetone has also been tested. Fig. 6.8 shows the response of the sensor to 100 ppm of ethanol, ammonia and acetone. The response of the sensor to ammonia and acetone is very low when compared to that for ethanol. Fig. 6.9 shows the time dependent response of the gases at room temperature for various concentrations from 5 to 100 ppm, at constant $V_g$ and $V_{ds}$ ($V_g=0$ mV and $V_{ds}=2$ V). The response and recovery times for the ethanol gas were found to be nearly equal i.e. from 50 s to 1 min. For lower concentrations of ammonia and acetone (5 ppm and 10 ppm) there is no considerable change in $I_D$. For 50 ppm of acetone, there is a slight response from the sensor which was also in the negligible range but the sensor has not shown any response to 50 ppm of ammonia. The sensor showed nearly equal but a smaller response to both ammonia and acetone gas molecules when their concentration was 100 ppm. The response is low when compared to that for 5 ppm of ethanol. Thus, the constructed transistor is more sensitive to ethanol than ammonia or acetone.
Humidity cross sensitivity of the constructed porous transistor has been tested by providing relative humidity (RH) up to 60% inside the sensing chamber. Various concentrations of ethanol vapours have been tested under the RH 60% as shown in the Fig. 6.10. The experiment has been carried out when the $V_g$ was maintained at 0 mV and $V_{ds}$ was at 2 V. There has been no observable change in the graph in Fig. 10 for the sensor tested at normal and humid conditions. But a slight change at a few data points has been noted in the collected data which are in the negligible range.
Fig. 6.8. Current-Voltage curves of the sensor recorded after exposure to 100 ppm of ethanol, ammonia and acetone vapours at $V_g=0$ mV.

Fig. 6.9 Response of the In$_2$O$_3$ sensor upon exposure to various concentrations of ethanol, ammonia and acetone vapours at room temperature, where $V_g = 0$ mV and $V_{ds} = 2$ V.
Temperature dependent sensing tests of the constructed transistor have been carried out by varying the temperature of the sensing element from room temperature to 50°C and 100°C. Fig. 6.11 clearly shows the improvement in the sensor response to ethanol at elevated temperatures. Here also the $V_g$ and $V_{ds}$ were kept at constant values ($V_g=0$ mV and $V_{ds}=2$ V). As the temperature increases from room temperature, the saturation point of the output current gets disturbed. Thus, it is inferred that if the constructed transistor has to be worked at elevated temperatures (i.e. above 50°C) the output signal has to calibrated to give a stable output.

Fig. 6.10. Humidity cross sensitivity of the sensor for various concentrations of ethanol.
Fig. 6.11. Temperature dependent response of the sensor to ethanol vapours when \( V_g = 0 \text{ mV and } V_{ds} = 2 \text{ V.} \)

To check the reproducibility of the constructed transistor sensor, four such sensing elements have been constructed with separately prepared coating solutions. The solutions were prepared with similar conditions as described in section 2.2.2. The Si-SiO\(_2\) substrates were dip coated at a constant dipping time of 1 min and annealed at 400ºC for 1 hr. Transistors have been constructed with the synthesized films and the sensing property of the constructed FETs was checked with 5 ppm and 10 ppm of ethanol vapours at room temperature when \( V_g=150 \text{ mV and } V_{ds}=1 \text{ V.} \) Fig. 6.12 shows the response of the constructed transistor sensors to ethanol vapours. All of the constructed FETs showed identical response to the ethanol vapours which confirms that the method adopted for the construction of transistor in the present work is reproducible.
The response of the constructed transistor to ethanol at room temperature was good when compared with that for ammonia and acetone. The response and recovery times of the sensor for ethanol were found to be nearly equal. The constructed sensor also showed good response to ethanol at elevated temperatures. However, if the sensor has to be worked at elevated temperatures, the observed disturbances have to be calibrated. The thin film transistor was selective to ethanol when compared to ammonia and acetone vapours. The reproducibility was also tested and proved. The selective detection of ethanol paves a way to construct a breath alcohol tester and with this result it is possible to construct a dedicated alcohol tester for checking human breath.
6.4. Thin film coating on modified glass substrates

6.4.1. Breath figure pattern

Nearly 100 years ago breath figures have been studied but had not elicited much attention before 1994. This method, also called as “moist-casting”, involves polymer casting from the solution under moist ambience [3]. Cooling of solution surface, caused by the solvent evaporation, enables condensation of water droplets on the surface followed by their growth and spontaneous ordering. Subsequent complete evaporation of both solvent and water results in the formation of 2D or even 3D arrays of air bubbles (droplet imprints), often ordered hexagonally, trapped in the polymer matrix. This technique of film structure formation appears extremely attractive, as it allows production of porous films (with pore sizes easily tunable by preparation conditions from 0.2 to 20 \( \mu \)m) that have numerous potential applications in biology, chemistry, and technology. Most of the previous experiments were performed for breath figures formed in an atmosphere of high relative humidity (RH>40%) which should be avoided in “high-tech” laboratories. Only very recently, it has been shown that breath figures can also be obtained in a drier atmosphere (RH=30%) by spin-casting polymer films from solutions containing small amounts of water [4]. Polymers, co-polymers, blended polymers, etc., all can be casted as films with breath figures [6, 5 and 3]. Breath figures can be prepared using polymethylmethacrylate (PMMA) by dissolving it in chloroform, tetrahydrofuran (THF) and Freon [6, 3 and 7].

In the present work, PMMA has been used to modify the glass substrate surface and the solvent used in the present work is THF.

6.4.2. Substrate surface modification and thin film coating

Initially, the glass substrates were cleaned using the procedure given in section 3.2.1. PMMA solution was prepared by dissolving PMMA beads in THF such that the molar ratio was 0.5M. Cleaned glass substrates were spin coated with PMMA solution. Spin coated glass substrates were then dried in a hot air oven at 80°C for 15 mins. While the solvent gets evaporated it leaves pores over the surface of the PMMA film (breath figures). Then, the prepared solution was spin coated on the PMMA modified substrates at 1000 rpm for 80 sec. After coating, the films were dried and annealed at 500 °C for 1 hour. While annealing the PMMA (m.pt. ≈150 °C), it gets
Modified substrate coating of thin films evaporated completely. Further, there is no role for PMMA in In$_2$O$_3$ nanostructured thin films. The formation mechanism of the film is shown in the Fig. 6.13.

![Diagram of film formation process](image)

Fig. 6.13. Mechanism of formation of algae-like growth of In$_2$O$_3$ thin films on glass substrates
6.4.3. Results and discussion

6.4.3.1. Structural analysis

Fig. 6.14 shows the XRD pattern of the annealed film coated on the modified substrate. This is in good agreement with the JCPDS file 06-0416 of the body centered cubic structure of In$_2$O$_3$. High intensity peaks are observed for (222), (400), (440) and (622) orientations. The average particle size calculated using Scherrer formula is 27 nm. The lattice parameter is found to be 10.11 Å which is in close agreement with the standard body centered cubic structure of In$_2$O$_3$ (JCPDS # 06-0416). The amount of strain present in the film is found to be $1.298 \times 10^3 \text{ lin}^2 \text{ m}^{-4}$ and the dislocation density of the film is calculated as $1.3742 \times 10^{15} \text{ lin/m}^2$.

![Fig. 6.14. XRD pattern of In$_2$O$_3$ thin film coated on polymer modified glass substrate](image-url)
6.4.3.2. Surface morphological analysis

Fig. 6.15(a) shows the SEM image of PMMA coated substrate. The surface is highly porous with pore size ranging from micro to nano size. Porous substrate is used for thin film coating and the coated and annealed film is shown in Fig. 6.15(b). While spin coating the solution over the porous substrates, the solution tends to move inside the pores and occupies the space available and the balance solution spreads over the surface. When the film is subjected to high temperature (i.e. annealing at 500°C) the polymer layer gets evaporated fully and leaves algae-like growth of film on the substrate. The surface roughness of the prepared thin film is observed through AFM analysis. Fig. 6.16(a and b) shows the AFM images of the surface modified substrate, which is highly porous as observed from the SEM image. Fig. 6.17(a and b) shows the AFM image of indium oxide thin film coated on the modified substrate, which is very rough and offers a larger surface area when compared to that on the unmodified substrate.

6.4.3.3. Gas sensing behaviour

In order to study the gas sensing behaviour of the prepared film, planar Al metal contacts were coated over the films by thermal evaporation. The constructed sensing element was placed inside the sensing chamber and the change in resistance of the films was analyzed by passing the test gas (ethanol) inside the chamber. The sensing phenomenon behind the gas sensing property of any metal oxide is the change in conductance / resistance of the material to the incoming gases. Sensor response was calculated using the formula,

\[ S = \frac{R_a}{R_g} \]

where \( R_a \) and \( R_g \) are the resistances of the sensing element in the presence of air and in the presence of reducing gases respectively. \( S \) is the sensor response of the material. There are only a few reports for room temperature sensitivity of metal oxides and in the current work, room temperature gas sensing properties of the nanostructured In\(_2\)O\(_3\) thin film were tested with reducing gases. Fig. 6.18 shows the sensor response for the reducing gas ethanol of the prepared sensing element, at room
temperature and 50°C. When the substrate temperature and gas concentration increases the sensor response also increases as shown in the inset of Fig. 6.18.

Fig. 6.15 (a) SEM image of PMMA coated on glass substrate and (b) SEM image of In$_2$O$_3$ thin film coated on modified substrate
Modified substrate coating of thin films

Fig. 6.16 (a) 2D and (b) 3D AFM images of PMMA coated on glass substrate

Fig. 6.16 (a) 2D and (b) 3D AFM images of PMMA coated on glass substrate
Fig. 6.17(a) 2D and (b) 3D AFM images of In$_2$O$_3$ thin film coated on modified substrate
6.5. Conclusion

Surface area of indium oxide thin film can be enhanced by dip-coating the prepared coating solution over Si-SiO₂ substrate and over polymer (PMMA) modified porous substrates. Surface analysis (SEM and AFM) of the thin films on modified substrates showed larger surface area when compared to the film coated on ordinary glass substrates. Sensor response of the constructed FET transistor and the sensing element prepared using modified substrates towards the reducing gas ethanol at room temperature is good. As the temperature increases from room temperature the sensor response also increases.
6.6. Reference


