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Enhancing Gas Sensing Efficiency of Isopropanol with Spin Coated WO_3 Thin Films

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Abstract

Utilizing Tungsten hexachloride(WCl6) as a solute and water as a solvent, pure and Ag-doped WO_3 thin films were successfully produced using the spin-coating process. GIXRD, SEM, EDX, and UV-Vis Spectroscopy were used to conduct structural, morphological, and optical analyses. The XRD pattern supports the formation of completely crystalline thin films. The formation of very uniform thin films can be validated using SEM micrographs. The band gap and thickness of the film were calculated using optical studies. Different Volatile Organic Compounds (VOCs) were used to investigate the gas sensing characteristics of thin films at various temperatures. At 120oC, an Ag-doped WO3 thin film performs exceptionally well against Isopropanol gas.

Key words: ***Tungsten hexachloride; Ag-doped WO_3; GIXRD; SEM; EDX; UV-Vis Spectroscopy; Isopropanol***

Introduction

Isopropanol is a clear liquid with a mushy, harsh odour. It is primarily used as a solvent in the coatings, pharmaceutical, home chemical, and electronic industries to clean printed circuit boards, as well as in other fields to remove oil, grease, and other handling soils. Isopropanol has a number of long-term health impacts in people, including lung cancer and the risk of developing foetuses in animals, but it also pollutes the environment [1]. As a result, rapid detection of the gas at low concentrations and lower working temperatures is required. The type of transducer utilised to convert the alcohol content information into an electric signal categorizes alcohol sensors.Many researchers are interested in semi conducting metal oxide materials because of its simplicity of fabrication, low cost, long-term stability, and potential to offer real-time monitoring.

Tungsten Oxide (WO_3) is a courier cathodic electro chromic material, whose colour turns to blue in its reduced state by inserting a proton or lithium ion when a reverse electrical potential is applied and turns to translucent at its oxidized state by extracting ions when a forward electrical potential is applied. There are many research reports about making tungsten oxide film coatings by a sputtering method, pulsed laser ablation deposition method, sol-gel coating method, electro deposition and spray pyrolysis methods. The sol-gel coating method uses tungsten chloride as a precursor coating solution and synthesizes tungsten oxide thin films by a dip coating or spin coating.Several research reports have attempted to obtain tungsten oxide thin films using WCl6 precursor solution and ammonium tungstate precursor solution.This study aims to synthesize tungsten oxide thin films by spin coating method. In this study, effort was made to obtain the polycrystalline phase of tungsten oxide by spin coating method.

Experimental

Material preparation

The amount of precursors *viz.*, WCl_6 is procured from Thermo-Fischer Ltd and $AgNO_3$ is procured from Sigma Aldrich were

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used to fabricate the thin films. WCl_6 and $AgNO_3$ were dissolved thoroughly in a mixture of 300mL of de-ionized water and 100 mL of NH3 solution along with 10 mL of HCl [2] to maintain the pH acidic. Prior to deposition, the substrates were ultrasonically degreased in a mixture of acid and water, rinsed in de-ionized water, then in acetone, and finally dried in air. The doping concentration of the precursor (as wt% of Ag) was taken as 2wt% and 5 wt%. The mixed solution was stirred for 2~3 hr and followed by ultrasonic agitation for ~30 min before usage.

$$WCl_6 + NH_3 + 3H_2O \rightarrow WO_3 + 6HCl + NH_3 \quad (1)$$

The solution was kept in dry air for 3 hrs with constant stirring. A small amount of each coating solution was dropped on the substrate, and it is allowed to spread over by spinning (2000 rpm, 20s) and dried at 250°C for 10 min. The same procedure was repeated several times to increase the film thickness. To prepare crack-free films annealing of every layer was done in air. Each layer was fired for 10 mins at 1000˚C before a subsequent coating. The final sol was pale yellow color for pure WO_3 and white color for Ag doped WO_3. This colour change can be attributed to the existence of $AgNO_3$. The obtained thin films are dark brown, homogeneous and adhere well to the substrate.

Gas sensing measurements

A static gas sensing approach was applied for the sensing characterisation of silver doped tungsten oxide thin films. A handcrafted testing spherical glass bottle with a capacity of 2L was used to test the samples for various volatile organic chemicals. From one side of the septum provided, a micro syringe was used to inject the required concentration of gas into the glass bottle. A digital thermostat and a compound heater were used to modulate and adjust the temperature. To construct ohmic electrical contacts on the film, thin copper wires and highly conducting silver paste were utilised. By detecting the change in electrical resistance in relation to the sensing response, an electrometer was utilised to record the sensing response [3]. The required gas concentration was achieved within the test chamber by injecting a prescribed volume of the test gas into the air tight chamber (volume = 2L), which was fixed to the surrounding air at atmospheric pressure. According to the alcohol densities and the volume of the chamber, the alcohol concentrations (250 ppm-2000 ppm) were estimated. The environment's relative humidity (RH) was 35-50 percent. The following formula was used to compute the gas's essential concentration using the static liquid gas distribution method.

(2)

where, D(ppm) is the target gas concentration, Ø is the required gas volume fraction, ρ (gml^{-1}) is the density of the liquid, V_1 (µl) is the volume of liquid, V_2 (l) is the volume of the chamber, and M (g $mol^{-}1$) is the molecular weight of the liquid. The sensor response (S) was calculated by the following equation:

(3)

where, R_{air} and R_{gas} are the electrical resistances of the sensor in the air and tested gas, respectively. The time of response and recovery has been defined as the time taken by the sensor to achieve 90% of the total voltage change in the case of adsorption and desorption, respectively. The schematic diagram of the gas sensing measuring circuit is shown in **FIG.1**. In the method of gas sensing examination the input voltage was set at 5V and the tuning of operating temperature of the gas sensor can be done by altering the Heater Voltage (VH). Test gas formed by evaporating the liquid that injected on to the bottom surface of gas chamber (bottom contain heater plate) by a micro syringe [4]. The output voltage was taken across virtual resistance which changes with sensor resistance. The sensor resistance is dependent on test gas and their concentration.

$$H \quad \frac{Co\mathcal{E}}{4}$$

Where β is the full width, which is half the maxima, λ is the wavelength of the X-ray (0.15406 nm), and θ is the diffraction angle. The average crystallite size of the as deposited WO3 is 39.68, 2% wt of silver-doped WO3 is 33.22, and 5% wt of silver-doped WO3 is 28.01 as shown in Table 1.

TABLE 1. **Crystallite and Microstrain of the samples.**

S.No	Doping Concentration	Crystalline size (D) nm	Micro strain(ε)
			(x10 m-3 m lines-2 m-4 m)
1	As deposited WO_3	39.68	0.18819
2	2 wt% Ag	33.22	0.13487
3	5 wt% Ag	28.01	0.12475

SEM

Scanning electron microscope could be handy approach to govern the morphology and particle size of the samples. **FIG. 3. (a)** and **FIG.3. (b)** indicate SEM image of Ag doped WO_3 nano particles. It is evident that each of the samples shows morphology with average diameter of 1 nm -1.5 nm and thickness of 180 nm-200 nm. The particle size approximate from XRD results is considerably under the SEM results. This swap in size is probably because of outsized particles which are composed of a lot of smaller particles. After doping of Ag the morphology lessen with an increase of Ag content. The decrease of crystalline size was additionally confirmed by XRD results.

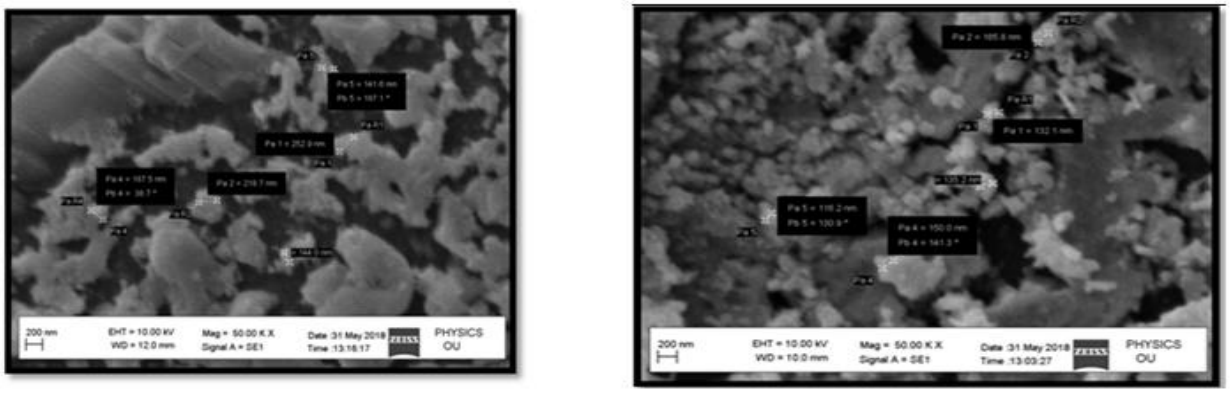

FIG. 3. **(a): SEM pictograph of 2wt% silver dsoped WO_3 thin films; (b): SEM pictograph of 5wt% silver doped WO_3 thin films.**

Optical properties

The optical properties of silver doped WO_3 thin film were characterized by UV-Vis transmission spectra analysis. It was perceived that the optical transmittance of the film was highly translucent with a pale yellow color and transmittance of over 80% in the visible light region. The transmittance spectra of the films for different doping concentration of Ag deposited with a film annealed at 500ºC. It is observed that increasing of the doping concentration of Ag shows the decreasing nature of transmittance. The Ag doping concentration gives the changes in the density of the unsaturated bonds, which resulted from the deviations in the density of localized states of the band gap. This may be the reason for the variation in transmittance. The drop in the transmittance of Ag doped WO_3 was chalked up to the increase in absorbance due to the occupancy of the metal ion. A substantial shift was observed in the absorption edges with the increase of Ag content from 2 wt% to 5 wt%, which suggests the decrease in band gap of WO_3 on doping as shown in **FIG. 4 (a) and FIG. 4(b)**. The transmittance of the films is decreased with incorporation in silver content there by increasing the film thickness, improvement of scattering, and absorption of light which gives rise to the band gap of tungsten oxide from and decrease in band gap from 3.14 eV to 2.42 eV.

FIG. 4. **(a): Absorbancy of silver doped WO_3 thin films; (b): Transmittance curves of silver doped WO_3 thin films.**

From the UV-visible spectra, the following relation is used to calculate the band gap energy (Eg).

(5)

The direct allowed transition is confirmed by the straight line portion as shown in **FIG.5(a)** and **FIG. 5(b)**. The band gap energy values are taken from the extrapolation of the vertical straight line of the plot to the photon energy axis (i.e., x-axis). By increasing the carrier density, the shifting of energy band with some of the W^{6+} ions replaced by Ag^{4+} ions resulted in a slight shift of the Fermi level into the conduction band. The band gap mainly depends on the electrons that excited to the Fermi level of conduction band from valance band. In agreement with earlier studies it was found that the energy band gap of crystalline tungsten trioxide to be approximately 2.4 eV, the films prepared by means of the sol-gel method. The optical band gap calculated by means of Tauc plot for indirect transition for the films drops. This kind of band gap narrowing was observed for their WO_3 films with the decrease of oxygen pressure, and set the behaviour to the oxygen deficient sub-stoichiometric WO_3-y which may be linked to the creation of profound localized states in the band gap.

FIG.5. **(a): Tauc plot of 2wt% silver doped WO_3 thin films; (b) Tauc plot of 5wt% silver doped WO_3 thin films.**

Gas sensing analysis

Metal oxide-based sensors typically work at high temperature (higher than 100). At those temperatures, the oxygen molecules are adsorbed at the surface (or, at temperatures higher than 2000°C, chemisorbed on the surface) and interrelate with target gas molecules, most important to elevated responses. In addition, high operating temperatures permit speedy response and recovery times.The process of detecting Isopropanol gas by WO_3 thin films can be explained as follows:

When the thin film is heated to ambient temperature oxygen is released from WO_3 thin film layer. The adsorption of the oxygen forms ionic species such as O^{2-}, O^{-2} and O^{-}.These oxygen species when desorbed results in increase or decrease of conductance

FIG.9. **(a): Response and recovery time of 2wt%silver doped WO_3 thin films (b): Response and recovery time of 5 wt%silver doped WO_3 thin films.**

Conclusion

The effects of silver doping, band gap, changes in particle size and film thickness and gas sensing parameters of the silver doped tungsten oxide film were studied. Silver can act as a promoter for the formation of tungsten oxide phases. XRD analysis shows that with increasing amalgamation of silver into the film, particle size decreases, deformation in the film decreases and the crystalline state increases. SEM images admit the presence of tungsten sub oxide phases in the film. Calculation of the band gap using the Tauc diagram shows that the band gap decreases as the silver content of increases. Compared to pure WO_3 silver doped WO_3 thin-film exhibited tremendous selectivity for isopropanol at operating temperature around 120°C. The improved sensing property can be due to potential barrier formed at interface between Ag and WO_3. The current dominant result establishes a new sensing mechanism available for gas sensors with high-quality performance.

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