Conference Paper

NO₂ Sensing Properties of WO₃ Thin Films Deposited by Rf-Magnetron Sputtering

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Tungsten trioxide (WO₃) thin films were deposited by Rf-magnetron sputtering onto Pt interdigital electrodes fabricated on corning glass substrates. NO₂ gas sensing properties of the prepared WO₃ thin films were investigated by incorporation of catalysts (Sn, Zn, and Pt) in the form of nanoclusters. The structural and optical properties of the deposited WO₃ thin films have been studied by X-ray diffraction (XRD) and UV-Visible spectroscopy, respectively. The gas sensing characteristics of all the prepared sensor structures were studied towards 5 ppm of NO₂ gas. The maximum sensing response of about 238 was observed for WO₃ film having Sn catalyst at a comparatively lower operating temperature of 200°C. The possible sensing mechanism has been highlighted to support the obtained results.

1. Introduction

Nitrogen dioxide (NO₂) is one of the most harmful gases to the ecosystem and provides a major contribution to air pollution [1]. The detection of NO₂ is crucial for monitoring environmental pollution resulting from combustion processes, particularly industrial emissions or vehicle exhaust [2]. Occupational Safety and Health Administration (OSHA, United States Department of Labour) declares the Permissible Exposure Limit (PEL) of NO₂ gas as 5 ppm for general industries and 20 ppm as Immediately Dangerous to Life or Health Concentrations (IDLHs) [3]. NO₂ gas is the main precursor for ozone layer depletion in lower atmosphere and also produces acid rain which is slowly damaging the ecosystem. Commercially, many NO₂ gas sensors are available in the market but they have poor sensitivity, high operating temperature, bulky size and are very costly. Thus, there is an urgent requirement of cheap, highly sensitive and selective NO₂ gas sensors which could be operated at lower operating temperature.

Gas sensors based on metal oxide semiconductors are used in a wide variety of applications including gas monitoring and detection applications [4–6]. Considerable research has been carried out on the development of chemical sensors based on semiconductor metal oxides such as SnO₂, ZnO, and TiO₂ because of their high sensitivity towards many reducing as well as oxidizing gases [7–9]. Tungsten trioxide has attractive electrical properties and reactivity to oxidizing gases making it one of the best candidates for gas sensing applications [10–12]. The tungsten trioxide (WO₃) thin films and nanostructures are seen to be an excellent candidate for NO₂ gas detection [13, 14] because the W transition metal is found to be with different oxidation states (W⁵⁺, W⁶⁺) enhancing the oxidizing power of NO₂ gas molecules onto the surface of WO₃ metal oxide. Thus, in the present work, WO₃ thin film based gas sensors have been exploited for the trace level (5 ppm) detection of NO₂ gas. Effect of different catalysts (Sn, Zn, and Pt) incorporated on the surface of SnO₂ thin film in the form of nanoclusters has also been studied for NO₂ gas detection.

TABLE 1: Deposition parameters for WO₃ thin film using Rf magnetron sputtering.

Target	W metal target (99.999% pure)
Substrate	IDE/corning glass; corning glass
Target to substrate distance	6 cm
Sputtering pressure	10 mT
RF power	50 Watt
Gas composition (Ar : O ₂)	60 : 40

2. Experimental Details

WO₃ thin film has been deposited by Rf-magnetron sputtering technique using a 2-inch W metal target (99.999% pure) in a reactive gas ambient of Ar and O₂ gas mixture. WO₃ thin films were fabricated onto the corning glass substrates patterned with Pt interdigital electrodes (IDEs). The description of fabrication of Pt IDEs has been mentioned elsewhere [9]. The typical growth conditions used for the deposition of WO₃ thin film are summarized in Table 1. WO₃ thin films were deposited under the growth pressure of 10 mTorr with argon to oxygen ratio of 60 : 40 by applying a Rf power of 50 W.

For the formation of nanocrystalline WO₃ thin film, in situ annealing was carried out at a substrate temperature of 400°C for 1 hour in 60% Ar: 40% O₂ environment. In order to get the enhanced sensing response characteristics, Sn, Zn, and Pt metal catalysts were incorporated onto the surface of WO₃ thin film in the form of nanoclusters on separate sensors. Sn, Zn, and Pt were also deposited using sputtering technique using their respective metal targets under the sputtering pressure of 10 mT and in 100% argon gas ambient. Nanoclusters of metal catalysts were deposited using a shadow mask of uniformly distributed pores of 600 μ m diameter onto the surface of WO₃ thin film. X-ray diffraction (XRD) study was carried out using Bruker D-8 X-ray diffractometer. Optical properties have been studied via UV-visible spectrophotometer (Lambda 35). WO₃ film thickness was measured using surface thickness profiler (DEKTA 150). Gas sensing characteristics of the prepared WO₃ thin film based sensors were studied in a specially designed "Gas Sensor Measurement and Calibration System (GSMCS)." Changes in the sensor resistance were recorded after every second using a digital multimeter (Keithley 2700) interfaced with computer. The sensing response of prepared WO₃ thin film based structures was calculated using the relation: $S = R_g/R_a$, where R_g is the resistance of sensor in the presence of target NO₂ gas and R_a is the resistance of the sensor in the absence of target NO₂ gas.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) spectra of WO₃ thin films deposited on corning glass substrate at a substrate temperature of 400°C. The XRD spectra show the formation of orthorhombic structure (JCPDS Card no. 35-0270) of WO₃ and do not show the presence of any other secondary phase indicating the growth of single phase and polycrystalline

FIGURE 1: XRD patterns of the WO₃ thin film.

WO₃ thin films. It is observed from Figure 1 that reflection corresponding to (002) plane is dominant and is relatively intense indicating preferential orientation of the deposited WO₃ thin film. The crystallite size calculated from the Debye Scherrer formula is found to be 17.73 nm which is relatively small leading to increase in grain boundaries suitable for gas sensing applications.

UV-visible transmission spectra of annealed WO₃ thin film deposited over corning glass substrate were measured in the wavelength range of 190 to 1100 nm and are shown in Figure 2(a). It can be seen that the film is highly transparent (88%) in the visible region showing good optical quality and low absorption losses. The presence of fringes at higher wavelength confirms that the prepared WO₃ thin film is free from any inhomogeneity. The onset of sharp fundamental absorption edge at about 310 nm was observed in the deposited WO₃ thin films (Figure 2(a)).

The Tauc plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (where α is absorption coefficient, h is planks constant, and ν is frequency of the incident radiation) of the WO₃ thin film deposited at 10 mT sputtering pressure is shown in Figure 2(b). Optical bandgap of the WO₃ thin film was calculated from the linear portion of the Tauc plot. Linear region is clearly seen in Figure 2(b) at $h\nu > 3.5$ eV for WO₃ thin film which is in accordance with the well-known absorption law $\alpha h\nu \sim (h\nu - E_g)^{1/2}$ being characteristic for direct optical transitions. Estimated value of bandgap of the WO₃ thin film is found to be 3.90 eV and is close to the reported value [15].

Figure 3 shows the variation of sensing response of all the prepared WO₃ thin film based sensor structures (WO₃, WO₃/Sn, WO₃/Zn, and WO₃/Pt) as a function of temperature towards 5 ppm of NO₂ gas. It is observed that the value of resistance of the sensors in the presence of air (R_a) increases to a higher stable value (R_g) when target NO₂ gas is inserted into chamber due to the oxidising nature of NO₂. When the NO₂ gas is flushed out of the chamber, all the fabricated sensors retain their original high resistance value (R_a).

FIGURE 2: (a) UV-visible transmittance spectra of the WO₃ thin film prepared on corning glass substrate. (b) Tauc Plot of WO₃ thin film.

TABLE 2: Sensor response, response time, and recovery time at their respective operating temperatures for the fabricated sensor structures.

Sensor	Sensor response	Operating temperature (°C)	Response time	Recovery time
WO ₃ /Sn	238	200	32 sec	15.3 min
WO ₃ /Zn	173	250	5.2 min	18 min
WO ₃ /Pt	118	270	4.6 min	17 min

FIGURE 3: Variation of sensor response with temperature for the sensor structures: WO₃/Sn, WO₃/Zn, and WO₃/Pt towards 5 ppm of NO₂ gas.

FIGURE 4: Variation of sensor resistance in air (R_a) with temperature for the sensor structures: WO₃/Sn, WO₃/Zn, and WO₃/Pt.

Figures 4 and 5 show the variation of sensor resistance in the presence of air (R_a) and in the presence of NO₂ gas (R_g), respectively, with temperature for all the prepared

sensors (WO₃/Pt, WO₃/Sn, and WO₃/Zn nanoclusters). It can be observed from Figures 4 and 5 that the value of R_a and R_g decreases with increase in temperature. When NO₂ gas interacts with the sensor surface at a particular

FIGURE 5: Variation of sensor resistance in the presence of 5 ppm NO₂ gas with temperature for sensor structures: WO₃/Sn, WO₃/Zn, and WO₃/Pt.

temperature, the value of resistance increases from R_a to R_g . The maximum increase in the value of R_g is observed for WO₃/Zn nanoclusters sensor structure; however, the higher value of R_a as compared to other sensor structures restricts the further enhancement in sensing response. Moreover, the maximum sensor response has been observed for WO₃/Sn sensor structure which may be attributed to the possible spillover of NO and O⁻ species onto the uncovered surface of WO₃ thin film. It can be observed from Figure 3 that the maximum sensing response of ~238 has been obtained for the WO₃/Sn sensor at a low operating temperature of 200°C. The obtained sensor response for all the sensors with response and recovery speeds at their respective operating temperatures is summarized in Table 2. It may be seen that the WO₃/Sn sensor exhibits comparatively high sensing response with fast response and recovery speeds at low operating temperature of 200°C. WO₃/Pt and WO₃/Zn sensors show a moderate response of 118 and 173, respectively, at high operating temperatures of 270°C and 250°C, respectively. For WO₃/Sn sensors, NO₂ gas reacts with free Sn sites as well in the similar way as with W sites and captures electrons thus giving a high sensor response [14]. NO₂ gas on interaction with Sn nanoclusters gets converted into NO and O⁻ species which spill over the WO₃ surface and captured electrons from WO₃ thin film thereby increasing sensing response.

4. Conclusion

The enhanced sensing response of 238 towards 5 ppm of NO₂ was obtained for WO₃/Sn sensor structure at a low operating temperature of 200°C as compared to other fabricated sensors, namely, WO₃/Zn, WO₃/Pt, and WO₃. Enhanced sensing response for WO₃/Sn sensor structure is attributed to the

spillover of NO₂ species over WO₃ surface thus enhancing the adsorption of NO₂ gas on the sensor surface that leads to an increased sensor response.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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