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Surface morphology dependent tungsten oxide thin films as toxic gas sensor

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ABSTRACT

Tungsten oxide (WO_3) films are of great importance in gas sensing technology due to its selectivity towards toxic gases. In this paper, structural, morphological and compositional properties of spray deposited and chemical vapor deposited WO_3 thin films were investigated using XRD, TEM, SEM, EDAX and Raman spectroscopy. These films have monoclinic crystal structure; and a filamentous network surface for spray deposited films whereas small flake-shaped microstructure was observed on the surface of chemical vapor deposited films. These films were studied for their gas sensing ability towards toxic gases like ammonia (NH_3) and sulphur dioxide (SO_2) as a function of temperature and concentration. Response-recovery characteristics were studied by varying gas concentration. The spray deposited films displayed higher gas response than the chemical vapor deposited films whereas the later exhibited lower optimum operating temperature as well as faster response and recovery. A correlation between the morphological, compositional, electrical and gas sensing properties of these films is also established.

1. Introduction

The environment is paying heavily for the air pollution caused by steep development of industries, automotive revolution and biological hazards. Further, the rapidly developing technology is posing a threat to the environment due to practices such as use of air conditioners, pipe gas, water heaters etc. which need proper gas-leak alarms. The issue of industrial pollution has to be given great importance and there is a necessity to stop environmental degradation associated to industrial growth. Unfortunately, we are lacking in this field and human lives are at stake. Therefore, it prompts to monitor the air quality for human health since the concentrations of hazardous gases in air are increasing. Under such circumstances, vital activities have to be played by all of us to save our environment from pollution. Few of them are eliminating those factory processes which cause substantial gas emission, limitation on working hours of such factories; promote sharing of vehicles, constant check on type and concentration of gases liberated in air using gas sensors etc.

Sulphur dioxide (SO_2) is a colorless hazardous gas with burning smell that causes various respiratory and cardiovascular diseases in living beings. It is also inimical to the environment as it causes hazardous acid rain [1]. Studies have linked the concentration of SO_2 to the exacerbation of conditions such as chronic bronchitis and emphysema [2]. Ammonia (NH_3) is useful in chemical industries, fertilizer factories, medical imaging, etc. however it is also a potentially toxic, polluting gas which causes severe irritation to eyes and respiratory system [3]. Hence, on-site detection of these toxic gases liberated from agricultural and industrial practices has become increasingly important in monitoring environmental pollution [4–6] which adversely affects the living world. In such conditions appropriate sensors can be made available as the bridge between the environment and the electronics to detect the target gas. Proper use of fabrication technology would lead to the inexpensive, reliable, robust and durable sensor.

A lot of attention has been attracted by metal oxide semiconductors as they are inexpensive, easily synthesized and ready-to-use gas sensors. These gas sensors have the property of varying the conductivity of the sensing material in the presence of a testing gas. The operating temperature of the sensor is very imperative and is dependent on the testing gas as well as the properties of the sensor material. Moreover the relation between gas adsorption and the particle size of the sensing material is also very crucial for its application as a gas sensor. To name a few, the commonly used sensing materials are tin oxide (SnO_2) and zinc oxide (ZnO) which detect toxic gases; however these suffer from limitations such as low reproducibility, selectivity and stability [7]. Along with these materials, tungsten oxide (WO_3) substantially responds to SO_2 and NH_3 gas [8–10]. Now-a-days researchers have become inquisitive towards WO_3 films owing to their tremendous potential of catalytic activity [11,12], gas sensing applicability [13,14], use in high-resolution flat display [14] and being an electro-chromic material [15]. WO_3 gas sensor has a worthy distin-

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guishability in terms of response to various target gases, responsiveness to doping, high chemical stability and low cost [16]. The fabrication techniques especially affect the surface properties and hence the sensing properties. WO_3 is therefore striking due to its ease-of-fabrication in thin film form using various methods. Certainly, particle size reduction is the main criteria in improving the gas sensing properties of semiconducting oxides and it can be achieved by various synthesis methods. WO_3 thin films can be fabricated by various techniques which include electron beam evaporation [17,18], thermal oxidation [19] and anodic oxidation [20] of tungsten, electrochemical deposition [21], hot filament chemical vapor deposition [22–24], sputtering [25,26] etc.

In the present investigation, we have made an attempt to synthesize WO_3 thin films using two techniques viz. Spray Pyrolysis Deposition (SPD) and Hot Filament Chemical Vapor Deposition (HFCVD) techniques. The fabricated WO_3 thin films were characterized for their structural, morphological features and are further tested for their gas sensing properties towards toxic gases such as SO_2 and NH_3. Relative study of the gas sensing properties based on the deposition techniques has also been supported.

2. Experimental

2.1. Synthesis and characterization of WO_3 thin films

Prior to the synthesis of tungsten oxide, the substrates (alumina and glass) were deposited with Gold (Au) using appropriate masking to print inter-digitated pattern as electrodes using thermal evaporation deposition technique. The Au inter-digitated pattern was about 300 nm thick; and both the width and the gap of the inter-digitated pattern was kept about 1 mm. The two ends of the Au electrodes were appropriately masked using a piece of alumina with proper clamping during the synthesis of tungsten oxide. Apart from being a noble metal, Au was chosen as a material of electrodes since it does not undergo oxidation readily at the temperatures set during the synthesis of WO_3 films by HFCVD and SPD techniques. It also has good compatibility with copper (Cu) contacts/wires used during gas sensing studies. The contact area of the film increases with such electrodes which helps in efficient conduction of semiconducting WO_3 film and that reflects in faster response of the sensor.

Tungsten Oxide (WO_3) powder (AR Grade, HPLC) was dissolved in Ammonia solution (AR Grade, 30% NH_3, Thomas Baker) using refluxing process at 60–70 °C for 2 h to prepare precursor solution of concentration 0.03 M. The solution was then sprayed on to electrode coated glass substrate at 450 °C using SPD technique with flow rate 15–20 lit/min to achieve uniform, well adhesive WO_3 thin film. Air was used as a carrier gas. Additional sintering of this thin film was not carried out. The resulting film appeared uniformly pale yellow in color which is the characteristic color of WO_3.

For synthesis of tungsten oxide thin film using HFCVD technique, high purity tungsten filaments were used as the parent material. The electrode coated alumina substrate ~1.5 cm x 1.5 cm were placed about 0.8 cm below the filaments. High purity H_2 and O_2 gases were flown over the heated W filaments at filament temperature (T_F) ~1800 °C with flow rates 100 sccm and 1 sccm respectively. Chamber pressure was maintained in the range 30–40 Torr and the substrate temperature (T_S) in the range 700–800 °C. At high filament temperature the W-filaments form an oxide layer over themselves which is sublimated due to its higher vapor pressure as compared to pure metal. Tungsten oxide evolved in the form of vapors reaches the substrate and gets deposited on it. Reduction of this as-deposited oxide into well adhesive pure W-film is carried out by hydrogen gas which is present in the gas mixture. In-situ conversion of as-fabricated W-film into its oxide was carried out by changing the gas flow rates of H_2 gas to 50 sccm and O_2 gas to 3 sccm at substrate temperature (T_S) ~ 500 °C for the duration of about 3 h. The resultant film was well adhesive and blue-grey in color. This blue-grey color is the indication of the formation of oxygen deficient tungsten oxide (WO_{3-X}) film [27] and hence suggests the requirement of higher concentration of oxygen during synthesis and/or longer oxidation time.

The structural characterization of these thin film samples was carried out using Bruker AXS D8 X-Ray Diffractometer (XRD), with CuK_α radiation and Renishaw InVia Raman Microscope. The surface morphology of the samples was studied using JEOL JSM 6360A Scanning Electron Microscope (SEM) and TECNAI G^2 20U-TWIN (FEI, Netherlands) Transmission Electron Microscope (TEM). The thickness of the films synthesized using the two different techniques was examined by Talystep profilometer and was found to be 2–3 µm.

2.2. Gas response measurements

The samples synthesized using both the deposition techniques were subjected to gas sensing studies towards toxic gases such as SO_2 and NH_3. The thin film samples were placed on a heater in an indigenously designed gas sensing setup consisting of a steel chamber provided with a gas inlet and a SELEC-PID-500 controlled heater assembly. The heater contained canthol wire as a heating element capable of reaching temperatures up to 500 °C with an accuracy of ± 0.1 °C. The temperature was measured using a standard K-type thermocouple. Copper wires were properly connected to Au electrodes. WO_3 thin film sensors were stabilized in air each time before gas sensing measurement was carried out in the range 100–300 °C. The change in I-V characteristics and hence the resistance of the WO_3 thin film sensors in the presence of toxic gases were recorded using Keithley 2400 source meter which was interfaced to a computer via GPIB. The gas sensing characteristics such as the gas response was calculated at different temperatures and the response-recovery transients towards the above mentioned gases for various concentrations were also recorded.

3. Results and discussion

3.1. X–ray diffraction studies

The XRD spectra of SPD and HFCVD WO_3 thin films were recorded in the range of 2θ = 20-35° and are shown in Fig. 1 in which the most intense peaks of tungsten oxide are observed. The diffraction peaks at angles 2θ = 23.1°, 23.6°, 24.3°, 28.7°, 33.2°, 34.1° correspond to diffraction planes (002), (020), (200), (112), (022), (202) respectively for both the samples and show the formation of monoclinic phase which is confirmed by card # 83-0951 of the standard JCPDS-ICDD data. The peak labeled as 'S' in case of HFCVD fabricated sample correspond to the underlying alumina substrate. Besides, there exists a minor difference in the pattern, crystallite size and intensity of the XRD peaks of SPD and HFCVD samples which indicate the effect of

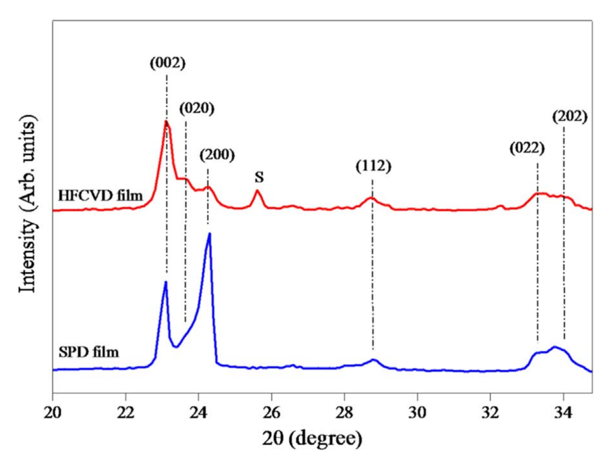

Fig. 1. XRD spectra of WO_3 films synthesized using SPD and HFCVD techniques.