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Nitrogen dioxide sensing properties of sprayed tungsten oxide thin film sensor: Effect of film thickness

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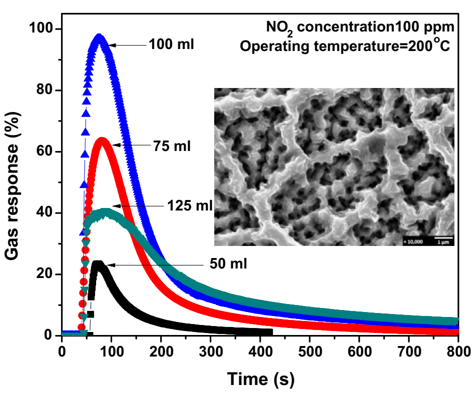
GRAPHICAL ABSTRACT



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ABSTRACT

We report a study on effect of film thickness on NO_2 sensing properties of sprayed WO_3 thin films. WO_3 thin films varying in thicknesses are deposited onto the glass substrates by simple spray pyrolysis technique by varying the volume of spray solution. Thin film gas sensors are characterized by using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM) and photoluminescence (PL) techniques to study their physical properties. Film having thickness 745 nm has shown highest gas response of 97% with 12 and 412 s response and recovery times, respectively towards 100 ppm NO_2 concentration. Gas response of 20% is observed towards 10 ppm NO_2 at 200 °C operating temperature. Sensitivity of the optimal sensor is 0.83%/ppm when operating at 200 °C with 10 ppm lower detection limit. The response of the sensor is reproducible and WO_3 films are highly selective towards NO_2 in presence of mist of various interfering gases viz. H_2S, NH_3, LPG, CO and SO_2.

1. Introduction

The perception of the surroundings based on mere senses is related closely to the progress of human/living being life. The smell or more specifically, the gas detection is a quite complicated sensorial practice which has an effect on human's decisions and actions. Humans are unable to detect number of gases such as CO, CO_2, CH_4, H_2, NO, NO_2 by smell above certain concentrations which can have fatal consequences if remained undetected and uncontrolled [1]. The massive usage of vehicles produce polluting gases such as CO, NO_x, SO_2, particles, and hydrocarbons [2] thus,

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it is obligatory to develop sensitive gas sensors to detect even sub-ppm of specific analyte gas in a complex gas mixture [3]. According to various studies done so far and available reports by the various environment monitoring/protection agencies significant air pollutants are O_3, NO_2, SO_2, CO, and particulate matter (lead) [2,4]. Among these pollutants risks to human lives due to NO_2 is high. When inhaled, NO_2 can be easily detected by its smell but at the same time, it is toxic. NO_2 detection by its smell is easiest way provided its concentration is below 4 ppm; otherwise it anaesthetizes the nose [5]. Thus, many times when NO_2 is leaked it remains unnoticed without use of some external sensing agency which may result in potential health risks. As far as NO_x sensing is concerned, WO_3 is the most popularly used material. Currently some of the WO_3 sensors are capable of measuring accurately in the 10 ppb range, which is well below the emergency exposure limit for human [6]. WO_3 nanowires were prepared by a vapour transport method using WO_3 powder as a raw material. The sensor made of the nanowires as thin as 50 nm showed the highest response towards 3 ppm NO_2 at a low operating temperature of 100 °C [7]. Irregular nanosheets of WO_3 have been prepared and high response to NO_2 even at sub-ppm level was observed by You et al. [8]. Using TeO_2 templates An et al. [9] synthesized WO_3 nanotubes and used for the detection of low NO_2 concentrations ranging from 1 to 50 ppm. A report discussing the effect of thickness variation of the WO_3 thin film on the NO response is available [10]. It is reported that thickness of the film affects the response and recovery kinetics of the sensor [11]. Dependence of the gas sensing performance on the thickness of thin films for various gases and materials is studied [12–17]. Desired thickness of the films is tuneable by controlling the preparative parameters. In spray pyrolysis method, by controlling the quantity of precursor solution to be sprayed, desired thickness of the thin films can be achieved.

We have made an attempt to develop a gas sensor based on WO_3 thin films deposited by simple spray pyrolysis technique. Variation in the thickness of the films has effect on various properties such as morphology, porosity, defects, composition, etc. and hence on the gas sensing behaviour. The effect of thickness variation on the physicochemical and NO_2 sensing properties of WO_3 thin films deposited by varying the film thickness is discussed in the present work.

2. Experimental

2.1. Materials synthesis

The substrates were cleaned by the procedure discussed elsewhere [18]. The peroxotungstic acid (PTA) of 0.5 mM concentration was prepared by dissolving (2.757 g) tungsten metal powder (AR grade, 99%; loba chimie Pvt. Ltd., Mumbai) in 30 ml of 30% hydrogen peroxide (H_2O_2) (AR grade; Thomas Bakers, Pvt. Ltd. Mumbai). The solution was initially kept in an ice bath for an hour to control the exothermic reaction. It is then rigorously stirred for 48 hours at room temperature until all the powder was completely dissolved according to reaction (1).

$$W + H_2O_2 + H_2O \rightarrow WO_3 \cdot nH_2O_2 \cdot mH_2O + \Delta \quad (1)$$

PTA thus formed was then diluted using double distilled water to 15 mM and used for the spray deposition. Thickness of the films was varied by varying solution quantity of the solution in four subsequent steps as 50, 75, 100, and 125 ml and the films were labelled as W_{345}, W_{675}, W_{745} and W_{801}, respectively according to their thickness (Table 1). PTA was sprayed on to the preheated glass substrates at optimized substrate temperature of 425 °C [19]. The nozzle to substrate distance was kept 28 cm and the spray rate was maintained at optimized value of 5 ml/cc.

2.2. Materials characterization

The deposited films were characterized by various techniques. To identify the crystal structure, the thin films were characterized by X-ray diffraction (XRD) technique and the diffraction patterns were recorded using Bruker D2 phaser X-ray diffractometer using Cu K_α radiation of wavelength 1.5406 Å. Monochromatic X-ray beam of energy 1253.6 eV was used in X-ray photoelectron spectroscopy (XPS) study (XPS, Physical Electronics PHI 5400, USA); which reveals information about chemical composition and valence state of the elements. Surface morphology and topography of the films were studied using scanning electron microscopy (SEM, Model JEOL JSM-6701F, Japan) and atomic force microscopy (AFM, Digital Instrument, Nanoscope III). Absorption spectra obtained from UV–Visible spectrophotometer (UV–vis 1800 Spectrophotometer, Shimadzu) was used to determine optical band gap. Room temperature photoluminescence (PL) spectra were recorded using Perkin–Elmer luminescence spectrometer model: LS55 to study the defects. Thickness of the films was measured by means of surface profiler (XP-1 Stylus Profiler, Ambios Technology Inc.).

Gas sensing measurements were carried out in locally fabricated gas sensing unit equipped with Keithley electrometer (6514). Sensor of size 1 cm × 1 cm was fabricated and silver contacts were drawn for good electrical contacts. Thin film sensor was mounted in 250 ml airtight container where it is preheated at required temperature using temperature controller. Sensor was heated until its resistance stabilized and the time required for this was around three hours. Thin film sensors were then exposed to the analyte gas of desired concentration in the gas sensor unit and change in the resistance was monitored using Keithley (6514) electrometer. After each successive measurement, fresh air was passed into the test box and then required amount of analyte gas was injected into the box to obtain a desired concentration. Selectivity studies were carried out by monitoring change in resistance of the film by purging various gases of desired concentration. Various canisters of CO, NH_3, SO_2, LPG, H_2S and NO_2 gases having 2000 ppm gas concentration were used as analyte gases procured from Shreya Enterprises Pvt. Ltd. Mumbai, Maharashtra, India.

3. Results and discussion

3.1. X-ray diffraction studies

XRD patterns of WO_3 thin films with different thickness along with the stick pattern of JCPDS card are presented in Fig. 1. XRD

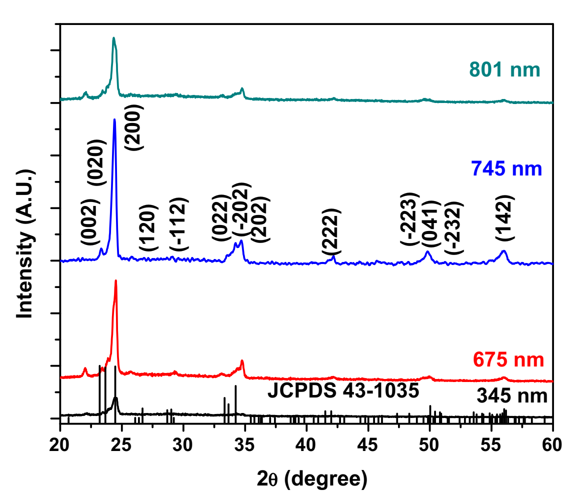

Fig. 1. X-ray diffraction patterns of WO_3 thin with different thickness.