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Influence of annealing temperature on nanostructured thin films of tungsten trioxide

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ABSTRACT

Tungsten trioxide thin films of ~300 nm thickness have been deposited on indium tin oxide coated glass and silicon substrates by thermal evaporation technique. Influence of annealing temperature on the structural, vibrational, morphological, optical and gas sensing properties of these films has been extensively studied to search out the possible applications in opto-electronic and gas sensing devices. From the studies of optical transmittance spectra it is observed that optical band gap decreases from 3.24 to 2.72 eV with increase in annealing temperature. It is also observed that because of annealing the photoluminescence yield of the films increases. All films, especially the annealed films have shown reasonably good gas sensing behavior in acetylene environment. The film annealed at 500 °C shows better optical as well as gas sensing behaviors and hence can have good device applications.

1. Introduction

Tungsten trioxide (WO_3) is one of the n-type indirect wide band gap semiconductors which have drawn a large amount of attention in the past decades from the theoretical and experimental point of view [1]. It has several interesting physical properties, such as electrochromic [2–4], photochromic [5], gasochromic [6], photo-catalyst [7] and photoluminescence properties [8]. Because of such outstanding characteristics, WO_3 films have been used to construct smart window, anti-glare rear view mirrors for automobiles, optical recording devices, solid-state gas sensors, humidity and temperature sensors, photonic crystals and so forth. Different authors have studied the sensitivity of WO_3 thin films to detect a broad range of oxidizing and reducing gases, such as NO_2 [9], NH_3 [10], O_3 [11], H_2S [12], CO [13] etc. with detection levels of a few ppm or less. Since WO_3 has a large indirect energy band gap, it also acts as a promising material for fabricating an ultraviolet (UV) photodetector [14]. Despite the spectacular progress reached by some of the technologies related to these properties, which in some cases resulted in commercial products, a corresponding deep understanding of the underlying mechanisms is still lacking.

The properties and applications of such materials are mainly governed by the crystal structure, chemical composition, and surface morphology, chemical and thermal stability of the resulting structures. A profound knowledge of these parameters is, therefore, of importance for its effective use in practical device applications. The preparation technique and its conditions play important role in tailoring the properties of the materials. Various techniques, such as thermal evaporation [15], chemical vapor deposition [16], sputtering [17], spray deposition [18], sol–gel processing [19], etc. have been utilized for deposition of WO_3 films. Thermal evaporation processing has good control over the microstructure and homogeneity of the coatings with less complicacy and for the present work we have grown our films using this technique. At the same

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time the characteristic behaviors of the films depend on the deposition technique used, the deposition conditions and the subsequent annealing process. Annealing, which is an essential process to obtain films with stable and well–defined microstructure, causes stoichiometric and microstructural changes. It has a high influence on the optical and gas sensing characteristics of the films too. In this paper we have investigated the changes in the morphology and structure in the WO_3 films prepared by thermal evaporation technique, followed by annealing at different temperatures in the range 200–600 °C. Different techniques like X–ray diffraction (XRD), Raman Microscopy and Atomic Force Microscopy (AFM) have been used to characterize the films. Optical and gas sensing properties of these films have also been studied.

2. Experimental

2.1. Preparation of WO_3 targets and films

Thin films of WO_3 were prepared by the thermal evaporation of pure WO_3 targets using a high energy electron beam (6 keV). The target was prepared in the shape of 10 mm diameter pellet using commercial grade WO_3 (99.9% purity) powder; the pellet was sintered using stepwise profile. First the heating rate was 2 °C/min, to a temperature of 500 °C from room temperature and held for 2 h, and then the heating rate was set as 1 °C/min to reach a temperature of 900 °C for 3 h in ambient air. Then the pellet was cooled down to room temperature at the rate of 1 °C/min.

WO_3 films were deposited on the glass substrates coated with indium tin oxide (ITO) and n-type Si (100) substrates by thermal evaporation of WO_3 powder extracted from the synthesized pellet; the powder was taken in water cooled Cu crucible. The substrates were cleaned with trichloroethylene, isopropanol, acetone and deionoized water before introducing it into the evaporator. The distance between the source to the substrates was ~20 cm and the base pressure in the evaporator was 5.6×10^{-7} Torr. Deposition rate was maintained as 10 nm/s using a quartz crystal balance and the thickness of all films was set as 300 nm. These WO_3 films were annealed at different temperatures 200, 300, 400, 500 and 600 °C for 1 h in oxygen atmosphere with temperature ramp of 2 °C/min.

2.2. Experimental setup for gas sensitivity measurement

The experimental chamber (Fig. 1) used for gas sensitivity analysis of the prepared films has been fabricated in house. It is made up of a hollow cylindrical stainless steel enclosure whose both ends are fixed with two circular perspex sheets (discs). The top sheet consists of two port holes for the insertion of gas inlet and sensor circuit, the holes are fitted with rubber rings to ensure zero leakage from the chamber. The chamber base is used for outlet of gas through vacuum pump. The flow rate of gas can be controlled by mass flow controller. As shown in figure, a heating coil is sandwiched between two copper sheets; the upper copper sheet is covered by a thin mica sheet for insulation, above which the film of dimensions 1 cm × 1 cm is kept. The heating coil and a thermocouple have been connected to a temperature controller in order to monitor the temperature of the film (though not used for this experiment as the paper deals with acetylene gas which is flammable). Two fine copper wires of approx 0.05 cm diameter have been placed approximately 0.8 cm apart on the film (with dimensions 1 cm × 1 cm) and fixed with silver paste for better contacts. A digital multimeter (Agilent 34401 A) and a source meter (Keithely 2400) have been used to measure the change in resistance of the film due to the presence of different amount of acetylene gas.

2.3. Characterization

Crystallographic characteristics of the films was examined at room temperature by a Bruker D8 Advance diffractometer using CuK_α radiation (0.15406 nm) at a continuous scan rate of 1°/min with resolution 0.1° for the range $20 \leq 2\theta \leq 60$ and step size 0.02. The surface microstructure was observed with the help of a "NT-MDT" (Molecular devices and tools for nano-technology, model no. P47–PRO) AFM; in contact mode with Si tips and at a scan rate of 1 Hz on the film area 5 μm × 5 μm. The Raman measurements in backscattering geometry were carried out at room temperature by a Reinshaw Invia Raman microscope system using Ar laser (514 nm) as the excitation source with spectral resolution 0.21 cm^{-1}/pixel. Optical transmittance spectra were measured using Shimadzu spectrophotometer (UV–2401 PC). Photoluminescence (PL) spectra were recorded using "HORIBA" PL spectrometer, where a xenon lamp (300 nm) was used as photon source. Small pieces of unannealed and annealed films with dimensions 1 cm × 1 cm were used for gas sensitivity measurements. It was a two probe measurement, probes being fine copper wires of approx 0.05 cm diameter were placed 0.8 cm apart on the film surface and fixed with silver paste for better contacts. A digital multimeter (Agilent 34401 A) and a source meter (Keithely 2400) were used to measure the change in the resistance. The measurements were carried out initially in absence and then in presence of different amount of acetylene gas at room temperature.

3. Results and discussion

3.1. Structural properties

The XRD patterns of our as–grown and annealed films are shown in Fig. 2(a)–(f). The as–grown WO_3 film at room temperature is amorphous in nature. Despite its simple stoichiometry, the structural transformations and phase transitions of WO_3 films are quite complex. We have thoroughly studied the crystallographic characteristics of our films using the 'Checkcell' software and the data of Joint Committee on Powder Diffraction Standards (JCPDS). The XRD data of the thin films annealed at 200–400 °C can be fitted well with monoclinic structure of space group *P2/m*; details of all cell parameters are listed in Table 1. It may be noted that the lattice parameters of the films annealed at 200 °C and 300 °C are almost same, but not exactly same for the film annealed