Applied Surface Science 362 (2016) 102–108

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Studies on growth and characterization of heterogeneous tungsten oxide nanostructures for photoelectrochemical and gas sensing applications

R. Senthilkumar[a], T. Mahalingam[b], G. Ravi[a,*]

[a] Department of Physics, Alagappa University, Karaikudi 630-004, India
[b] Department of Electrical and Computer Engineering, Ajou University, Suwon 443-749, South Korea

ARTICLE INFO

Article history:
Received 4 August 2015
Received in revised form 8 November 2015
Accepted 16 November 2015
Available online 1 December 2015

Keywords:
Thermal evaporation
Tungsten trioxide
Heterogeneous nanostructures
Photochromic
Gas chromic

ABSTRACT

Tungsten oxide nanostructures were developed on indium tin oxide coated glass substrates by modified thermal evaporation process without using catalyst and vacuum. Depending on the substrate temperature and vapor concentration, different nanostructures like rod, sheet and pyramid were formed. Morphology, phase structure and crystallinity of the nanostructure films were characterized by Scanning electron microscope (SEM), X-ray diffraction (XRD), Raman spectroscopy and HR-TEM. The samples were investigated under dark current and photocurrent and in H_2SO_4 aqueous solution as a function of applied potential. The saturated photocurrent density of tungsten oxide was found to be ≈14.4 μA cm^{-2}. The films were also investigated as resistive gas sensor for ethanol gases (10–50 ppm) at room temperature. The response and recovery time were also determined.

1. Introduction

Metal oxides such as MoO_3, WO_3, V_2O_5, TiO_2 and SnO_2 play vital role in many areas of physics, chemistry and material science. Among the metal oxides, tungsten oxide (WO_3) is an ideal material for applications in optoelectronic, photovoltaic devices and also in biological and chemical sensors [1–4]. The nanostructured formation of WO_3 thin film exhibits excellent photoconductive and gas sensing properties. The photoresponse of WO_3 nanostructures is found to be quite useful in understanding electrical and surface related properties. Tungsten oxides are identified to exhibit large gas sensitivity, faster response time and low working temperature for the detection of various toxic gases such as H_2, NO_2, H_2S, NH_3, O_3 and hydrocarbons. The detection of H_2 is very important because its extremely flammable nature causes fire and explosion. The higher concentration of H_2 arises oxygen deficiency and causes abnormal breathing (asphyxia) for human being and damages to skin and other tissues (frostbite) at freezing stage. The development of hydrogen sensors with high stability, sensitivity and fast response are highly desired [5–7]. Hydrocarbon vapors are essential in the domestic sector, which includes CH_4, liquid petroleum gas (LPG), and ethanol (C_2H_5OH) which causes major hazards to human being. Among these, ethyl alcohol is one of the most important gases to be identified due to its toxic nature [8]. The toxic gas sensing ability of WO_3 material is monitored based on the variation of its electrical resistance. Simple room temperature gas sensors are required to sense the presence of ethyl alcohol, because their evaporation temperature is very low.

A number of techniques are reported for the deposition of WO_3, including pulsed laser deposition, thermal evaporation, sputtering, spray pyrolysis, chemical vapor deposition, hydrothermal, and electrodeposition [9,10]. Among these techniques, the deposition of WO_3 using thermal evaporation technique tender great advantages as it could yield highly crystalline monoclinic structures. In this technique, surface morphology of WO_3 is found to be strongly dependent on the substrate temperature and source vapor concentration conditions. Few authors have reported the synthesis of tungsten oxide from tungsten plate as source or substrate by using tubular furnace with vacuum system and catalysis [11–13]. Through the present study, we have reported the synthesis of nanostructured tungsten oxide film on ITO coated glass substrate without using catalysis and vacuum by horizontal tube furnace under simple thermal evaporation technique. The film was characterized by X-ray diffraction (XRD) analysis using a PANalytical

* Corresponding author. Tel.: +91 04565 225206; fax: +91 04565 225202.
E-mail addresses: raviganesa@rediffmail.com, gravicrc@gmail.com (G. Ravi).

http://dx.doi.org/10.1016/j.apsusc.2015.11.150
0169-4332/

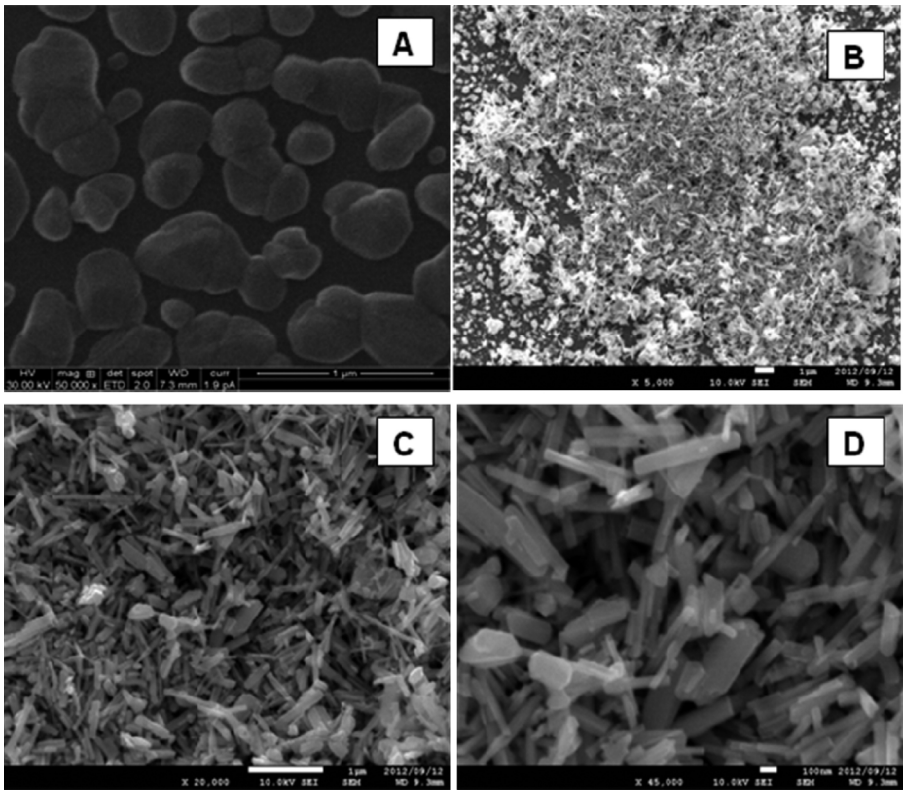

Fig. 1. FESEM images of (A) Islands of tungsten oxide vapors, (B) immense paddy growth and (C, D) antistrophic nanorods.

model X'PERT-PRO X-ray diffractometer system with the Kα radiations from a copper target (λ = 1.5418 Å). The morphology were examined using a scanning electron microscope (SEM) (JSM 6390F, JEOL/EO) and transmission electron microscope (TEM) (JSM 6390F, JEOL/EO). Raman spectrum was recorded using an imaging spectrograph STR 500 mm focal length laser Raman spectrometer (SEKI, Japan). Photoelectrochemical and gas sensing properties were further investigated and discussed.

2. Synthesis of WO_3

Nanostructures of tungsten oxide are synthesized by modified thermal evaporation process using a quartz tube kept in a single zone horizontal tubular furnace (Thermolyne-4700) without vacuum and catalysts. 2 g of tungsten trioxide source material (Sigma Aldrich, purity 99.997) was sprinkled in an alumina boat and then placed at the centre of the quartz tube. An indium tin oxide coated glass (Sigma Aldrich, sheet resistance 45 Ω/sq) substrate ($10 \times 10 \times 1\ mm^3$) was positioned at 20 cm distance from the source along one side of the quartz tube. Then, the reaction tube was purged with argon inert gas. The temperature of the tubular furnace was increased at a constant rate of 7 °C/min from room temperature till it reach to 1100 °C. After attaining that constant temperature, oxygen-argon gas mixture (O_2/Ar) was admitted through another end of the quartz tube in different sccm ratio and maintained for 6 h. Next, the temperature of the tubular furnace was decreased at a constant rate of 30 °C/min from higher temperature to room temperature [14,15]. During this process, tungsten trioxide powder was heated and it produced vapors at elevated temperature. These vapors were transported through carrier gas and deposited directly on ITO glass substrates kept at low temperature region to form nanostructured film.

3. Results and discussion

3.1. Morphological analysis

Scanning electron micrographs showed the formation of well defined structures including one dimensional (1D) nanorods, three dimensional (3D) nanosheets and truncated pyramids. The sizes of these structures are approximately 0.5–1.6 μm, 0.5–2 μm and 1–2 μm in length, 20–70 nm, 70–100 nm and 2–3 μm in diameter, respectively. Various types of nanostructures observed in WO_3 films grown on ITO depends on factors such as source and substrate temperature, the pressure, and the concentration of growth species in vapor solid growth. Generally, vapor concentration and substrate temperature play important roles in controlling the nucleation and growth of WO_3 nanostructures [16]. During the synthesis of WO_3 nanostructured thin films, vapors are produced by heating tungsten oxide powder at 950–1100 °C temperature and transported to lower temperature zone (350–420 °C) using argon carrier gas and oxygen mixture (25/75, 50/50 and 75/25). Subsequently, the vapors are deposited on the ITO substrates. The vapors may be adsorbed or de-adsorbed onto ITO substrate for the growth of crystal structure as shown in Fig. 1(A). Next, the adsorbed island species undergoes a surface diffusion which includes a growth site and continues connecting the islands to form immense paddy growth on the substrates as shown in Fig. 1(B). These massive growths are one-dimensional nanostructures that lead to anisotropic growth, where the crystal grows faster along certain orientations than others as shown in Fig. 1(C). In the presence of lower vapor concentration, the source gets insufficient oxidation in gaseous state resulting in the formation of nanorods on the substrate. The newly arriving molecules from the source are low which leads the growth in one direction as shown in Fig. 1(D) [17,18]. It is evident that the source temperature and vapor concentration influences the morphology