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Optimization of tungsten oxide films electro-deposited on macroporous silicon for gas sensing applications: Effect of annealing temperature

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Abstract

Polycrystalline WO_3 films grown on macroporous silicon via electrochemical deposition, have been studied as a function of annealing temperature. The hybrid structure was characterized using scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and Fourier transform infrared spectroscopy. The microstructure and grain-size of the metal oxide film were found to have significant influence on its electrical and sensing properties. DC conductivity measurements reveal the rectifying behavior of the junction, which is found to increase with annealing temperature. The increased sensitivity of the samples annealed at 700 °C has been attributed to a lower grain size, which contributes to an increase in the depletion region per unit length. An extrapolation of the variation of the resistance $\Delta R/R_0 = 1.5\%$ predicts possible ethanol sensing up to 1 ppm.

Keywords: Electrodeposition; Gas sensing; Macroporous silicon; Tungsten oxide films

1. Introduction

Transition metallic oxides have attracted attention as sensor materials due to their sensitivity towards different kinds of gases [1–4]. Among the different metal oxides, tungsten oxide (WO_x; this nomenclature is used due to fact that tungsten oxide is a sub-stoichiometric material) is very popular due to its wide band gap and is found to be very useful in areas such as sensing, catalysis, electrochemical industry and field emitters [5–7]. Apart from this, WO_x possesses electrochromic, optochromic and gasochromic properties [8], which have been applied to design smart windows, electrochromic displays, etc. [9]. In the recent past, scientific community is aggressively looking for cheap, reliable and high-performance sensors for monitoring different gases. Tungsten oxide is an important semiconductor and is considered as one of the most promising materials for sensing applications. Furthermore, this semiconducting material can be fabricated in thin films to optimize its properties, i.e., to minimize the size of the devices and to integrate with the silicon technology [10].

WO_x thin films can be prepared by various techniques [11–14] and under different processing conditions, the films usually possess different microstructures and properties. In the recent years, tungsten oxide 1D nanostructures have been mainly grown on silicon or tungsten substrates [15]. Different types of porous substrates have also been used for improving the sensing response of WO_x, e.g. porous alumina [16] or macroporous silicon (MPS) [17].

In particular porous silicon (PS) has various interesting properties for sensing applications, such as variable surface chemistry and high chemical reactivity [18,19]. Apart from these properties, it has open structure (pores) and large surface area. In general, the versatile nature of PS makes it an ideal

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substrate for potential applications in the field of optoelectronics, photovoltaics, gas sensors, photonics and biomedical applications [20–24].

Several studies of WO_x deposited on silicon have been reported, e.g. Fang et al. [25] reported WO_x films with different stoichiometries, deposited on Si(111) wafers by pulsed laser deposition technique; Galléa et al. [26] investigated the growth process of WO_x nanostructures deposited on Si substrates by a thermal oxidation and constructed a phase growth diagram with the possibility to realize the phase selection and morphology control of WO_x. Recently Yan et al. [27] synthesized WO_x nanoparticles by sol–gel method and deposited it onto the porous silicon and alumina substrates by dip-coating. Gas sensing tests experimentally demonstrated an improved NO_2-sensing with PS substrates decorated with WO_3 nanoparticles, as compared to WO_x deposited on alumina or pristine/pure PS. The same group [28] prepared n-WO_{3-x}/n-PS junctions (by sputtering) for NO_2 sensing. The sensor exhibited a strong response, fast response/recovery rate, excellent repeatability and good selectivity for efficient detection of NO_2 at ppb level. Finally, our group [29] has recently studied optical and structural properties of WO_x electrodeposited on luminescent meso-porous silicon resulting in an increase of photoluminescence intensity with annealing temperature under nitrogen atmosphere in contrast with air atmosphere.

Ma et al. [15,16,28] have grown different morphologies of tungsten oxide onto MPS for gas sensing application using an expensive, complex and time consuming technique for such deposition [27]. In the present work, optical, structural, electrical and sensing properties of WO_x films, deposited onto the MPS substrate through inexpensive, facile and rapid technique (i.e. electrodeposition), have been studied as the function of annealing temperature.

2. Experimental

2.1. Preparation of porous silicon

MPS was formed by an electrochemical etching of (100)-oriented, boron-doped p-type silicon substrates of resistivity 14–22 Ω cm, using an electrolyte consisting of 4 wt% hydrofluoric acid (48 wt%) in N'N-Dimethylformamide (ACS reagent, ≥ 99.8%). The current density during anodization was kept at 6 mA/cm^2 for 1 h. After fabrication, the samples were rinsed with N'N-Dimethylformamide (DMF) and dried with slow nitrogen flux.

2.2. Electrodeposition of WO_x

Thin films of WO_x were obtained by electrodeposition in a peroxytungstic acid solution contained in an electrochemical cell with a platinum mesh as the auxiliary electrode and MPS as the working electrode. The working electrode was subjected to a constant cathodic potential of 10 V with different deposition time of 20 and 30 min. The obtained WO_x films were homogenous, stable and transparent. Effect of heat treatment on the hybrid structures was studied at 500 and 700 °C for one hour under air atmosphere.

Structural properties of MPS and its composite with WO_x were analyzed using a scanning electron microscope (SEM) Hitachi VP-SEM SU1510. The orientation and crystallinity of WO_x was analyzed by XRD (Xpert'PRO) using CuKα radiation having wavelength of 1.54 Å. Fourier Transform Infrared spectroscopy (FTIR) model Cary 660 was used for obtaining the information about the chemical bonds formed in the composite structure. The transport characteristics were studied with the help of DC resistance measurements through the lateral and transverse configuration. The gas sensing measurements were carried out in homemade static gas sensing characterization system with the ability to control the ethanol concentration through mass flux-meters. PPM concentration in the chamber was calculated by the pressure variation using a pirani gauge. To confirm the presence of oxygen vacancies, tungsten oxide powder from Sigma Aldrich of 99.9% purity was used as a reference.

3. Results and discussion

Fig. 1 shows top and cross-sectional SEM micrographs of as prepared MPS. These images reveal a uniform surface and squared/rounded shape pores of ~1 μm diameter (see inset in Fig. 1a). The corresponding cross-sectional images showing the macroporous structure of the PS layer is shown in Fig. 1b. The silicon wafers were etched for 60 min for the formation of ~28 μm thick porous layer.

Fig. 2 shows the top and cross-sectional SEM images of some hybrid structures (MPS–WO_x). It is a granular structure distributed all around the pore walls. Magnified view is shown as inset in Fig. 2c. An increase in the deposition time from 20 to 30 min resulted in the formation of some agglomerates on the porous surface as well. The presence of WO_x throughout the pore depth was confirmed by energy-dispersive X-ray spectroscopy (EDS) analysis given in the latter part of the manuscript.

Fig. 3 shows the top and cross-section view of WO_x–MPS composites after annealing at 500 and 700 °C respectively for 1 h under air atmosphere. WO_x is found to cover the pore walls and the adhesion of WO_x along the pore depth in the form of thin film is a common feature at both the annealing temperatures. Other notable difference observed at 700 °C is the accumulation of WO_x at the bottom of pore (encircled in Fig. 3d). Formation of WO_x agglomerates at the bottom of the pores at 700 °C possibly results in the thin WO_x layer left on the pore walls.

FTIR is a technique used to obtain information about the chemical bonding in a material. The FTIR spectra taken through an attenuated total reflectance (ATR) accessory of as-deposited and annealed WO_x–MPS hybrid structures are shown in Fig. 4. The spectra of as-deposited WO_x films (Fig. 4a) reveal absorption bands at 541 and 560 cm^{-1}. Such values are slightly shifted compared to the bands at 550 and 572 cm^{-1}, which have been shown in WO_3 films fabricated by the sol–gel technique and correspond to the peroxo groups W–O–O stretch modes [30]. Fig. 4a also presents a band at 608 cm^{-1}, which is displaced from 612 cm^{-1} and can be assigned to the O–W–O stretch, typical of crystalline hydrated