Effect of annealing temperature on nanostructured WO$_3$ films on P-Si substrate

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Abstract

Nanostructured WO$_3$ films are prepared on p-Si substrate by facing target sputtering (FTS) method with sputtering pressure, 0.1 Pa and 200W. The sample is annealed at 850°C in air with 5°C/min. The as-deposited and annealed WO$_3$ films have been characterized by the Grazing incidence X-ray diffractometer, Field emission electron microscopy, and Ultraviolet-visible spectrophotometer. The surface morphology of the WO$_3$ films strongly depends on the annealing temperature. An average diameter of the WO$_3$ nanorod is 5-6 μm long and 800 nm diameter. It is revealed from optical study that the band-gap energy of WO$_3$ films is around 2.85 eV. The surface morphology of nanostructured WO$_3$ films has been discussed with the increase of annealing temperature.

1. Introduction

Hierarchical self-assembly of nanosized building blocks, including nanowires, nanobelts, nanoplatelets, nanotubes, etc. is an important process for the fabrication of functional electronic and photonic Nanodevices[1]. In this regard, remarkable progress has been made for the synthesis of complex inorganic materials with controlled architectures, sizes, morphologies, and patterns since these parameters represent key elements that determine their electrical and optical properties [2]. Among transition metal oxides, tungsten trioxide (WO$_3$) is of great interest and has been investigated extensively due to its many interesting structural and defect properties. Numerous applications of WO$_3$ optical and electronic based devices include...
electrochromic (EC) smart windows, flat panel displays, tunable EC photonic crystals [3], gas sensors[4, 5], water splitters, dye sensitized solar cells and batteries. For the fabrication of many of such devices and increasing their efficiencies, nanostructured WO3 films are required to be “thick and porous” enough to provide sufficient volume for producing high interaction areas. Besides, synthesis and assembly of “specific crystallographic phase” can further improve the characteristics of WO3. Tungsten oxide (WO3) is an n-type semiconductor and has been investigated extensively owing to their promising physical and chemical properties [6]. WO3 shows good optical properties and proper chemical stability; that is, Eg in the range of 2.5–2.8 eV (λ of 400–450 nm) is very suitable for the energy region of visible light [7, 8]. The synthesis of one-dimensional (1D) nanostructures and the assembly of these nano meter-scale building blocks to form ordered superstructures or complex functional architectures offer great opportunities for exploring their novel properties and for the fabrication of nanodevices [9]. Thus for several techniques for the preparation of 1D tungsten oxide nanostructured films have been developed [6].

The deposition of WO3 nanostructured films by facing targets sputtering technique is the newest fabrication method of thin films, with lower particle bombardment compared with the RF sputtering and DC sputtering, because of its special target arrangement. The FTS apparatus are very effective systems for depositing high quality thin films because plasma perfectly confines by the magnetic field between two targets. The thin films can be deposited in non-bombardment by electron (“damage free”) conditions [10-12].

In this work, nanostructured WO3 films have been deposited on Si-based substrate by using FTS method with sputtering pressure of 0.1 Pa and annealed at 850°C. The structural, surface morphological properties of nanostructured WO3 films have been investigated and discussed.

2. Experimental section

The FTS systems in our laboratory for preparing WO3 thin layer is shown in Fig. 1[13]. The distance between the target-to-target, and the center of the targets’ to the substrate were 100 mm and 50 mm, respectively. W rectangular plates (having 115 x 75 mm, thickness of 3 mm and purity of 99.95 %) were used as targets. The chamber was evacuated to a vacuum level of 7×10⁻⁴ Pa. The WO3 nanoparticles were deposited reactively on Si-based substrate for 2hrs at DC input power of 200 W with sputtering pressure of 0.1 Pa and a fixed Ar to O₂ gas ratio (G_R) of 6:4 [14]. As-deposited WO3 nanoparticles are annealing in a muffle furnace (TMF5, Thomas) under oxygen environment at 850°C for 2hrs, because as-deposited films are the amorphous structure. The thickness (2 μm) of the WO3 films was determined with a mechanical surface roughness meter (SURFCOM Accretech, 1500 DX) using the step between film and substrate. The crystal structures of the TiO2 films were determined by grazing incident X-ray diffraction (GIXRD) spectra (SHIMADZU XRD-6000) with Cu-Kα line. The data were recorded from 2θ values 20° to 80° with a step of 0.02. For GIXRD measurement incident angle was fixed at 0.45°. The optical properties of the films (prepared on glass substrate) were measured with JASCO V-550 spectrophotometer at room temperature within the wave length range 300-900 nm. The surface morphologies were studied using field emission scanning electron microscope (FE-SEM) with Model: JEOL, FE-SEM 6700F.
3. Results and discussions

Figure 2 shows the GIXRD patterns of as-deposited and annealed WO₃ thin film prepared on Si-based substrate. The GIXRD patterns of the as-deposited WO₃ films are found to be amorphous in nature, but crystalline films were obtained when the film is annealed at high temperatures of 850 °C. The lines located at 23.12°, 23.6°, 24.28°, 28.80°, 47.24°, and 50.52° are assigned to the lattice plane reflection of triclinic WO₃ phase with lattice parameters \( a = 0.7311 \) nm, \( b = 0.7515 \) nm, and \( c = 0.7679 \) nm (PC-PDF No. 83-0948). However, triclinic and monoclinic diffraction peaks almost overlap for many \( 2\theta \) values and it is difficult to discriminate between these two phases. On the other hand, according to the phase diagram, the monoclinic and triclinic structures are the most common and coexist in WO₃ at temperatures higher than 500 °C [15]. The crystallite size of the particles has been estimated from the Debye–Scherrer's equation using the GIXRD line broadening as follows [16]:

\[
D = \frac{0.94\lambda}{\beta \cos \theta},
\]

where \( D \) is the crystallite size, \( \lambda \) is the wavelength of the X-ray radiation (Cu K\( \alpha \)=0.15406 nm), \( \beta \) is the diffraction angle and \( \beta \) is the FWHM. A finite diffraction peak has been chosen for calculation of crystallite size. The diffraction peak (002) has been chosen for calculation. The derived grain size is 12.3 nm for the annealed WO₃ thin films.

![Fig.2. The GIXRD patterns of as-deposited and annealed WO₃ thin films](image)

![Fig.3. The optical transmittance spectra of as-deposited and annealed WO₃ thin films](image)

Figure 3 shows the transmittance spectra as a function of wavelength (300 - 800 nm) for as-deposited and oxygen-annealed WO₃ thin films, prepared in same conditions. The spectra of as-deposited WO₃ films show the usual interference pattern in the range of low absorption with a sharp fall of transmittance at the band edge. The oxygen-annealed WO₃ thin
The oxygen-annealed WO$_3$ films have less interference. It has been observed that the transmittance edge shows the red-shift with the oxygen-annealed WO$_3$ films. It is may be due to the high crystallinity, observed within the sample of investigation. The average transmittance in region varies from 78% to 60.5% with as-deposited and annealed WO$_3$ films, respectively.

We assume an indirect transition between the top of the valence band and the bottom of the conduction band in order to estimate the optical band gap ($E_g$) of the films using the relation [18]:

$$
\alpha(h\nu) \propto A(h\nu-E_g)^2,
$$

where, $\alpha$ is absorption coefficient, $A$ is the edge width parameter and $h\nu$ is the photon energy. Figure 3 shows the plots of $(ah\nu)^{1/2}$ versus the photon energy of the films grown at different sputtering powers. The optical band gap of the films was determined from the extrapolation of the linear plots of $(ah\nu)^{1/2}$ versus $h\nu$ at $a=0$. The optical band gap of the films is 3.04 and 2.85 eV for as-deposited and annealed WO$_3$ films, respectively.

![Fig.4. $(ah\nu)^{1/2}$ versus energy for as-deposited and annealed WO$_3$ thin films.](image)

![Fig. 5. FE-SEM images of as-deposited and annealed WO$_3$ thin films.](image)

Figure 5 shows the surface structure and morphology of as-deposited and oxygen-annealed WO$_3$ films. From the Fig. 5(a), the as-deposited films have a smooth surface and nanograins are observed in a larger magnification, which reaffirms their amorphous nature. The average-size of the nanograins is 13-17 nm. Oxygen-annealing of the films at 450 °C not only manifests in enhancement of particle size but also in a considerably different surface morphology. It is cleared from the Fig.
5(b) that the whole surface of this film is covered by nanorods and rectangular nanostructures. The average-size of each nanorod is approximately 5-6 μm long and 800 nm diameter. The rectangular shape has cross-section of ~750x~750 nm.

4. Conclusion

The nanostructured WO₃ films were successfully deposited on Si-based substrate by FTS method with sputtering pressure of 0.1 Pa and annealed at 850°C. High crystalline film is achieved with annealed at high temperature. The whole surface is covered with nanorods and rectangular nanostructures. As-deposited WO₃ films have amorphous structure. For the annealed WO₃ films, the average-size of each nanorod is approximately 5-6 μm long and 800 nm diameter. The rectangular shape has cross-section of ~750x~750 nm. This nanostructured WO₃ films can be used for photocatalytic, electrochromic and solar cells applications. The efficiency of these devices may be enhanced by increasing the thickness of WO₃ films.

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References