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Fabrication and characterization of optical and electrical properties of vanadium doped titanium dioxide nanostructured thin film

Mahla Asgharinezhad^a, Akbar Eshaghi^{b,*}, Ali Arab^a

^a Department of Physics, Faculty of Applied Sciences, Malek Ashtar University of Technology, Shahin shahr, Esfahan, Iran ^b Faculty of Materials Science and Engineering, Malek Ashtar University of Technology, Shahin shahr, Esfahan, Iran

ARTICLE INFO

Article history: Received 9 April 2016 Accepted 1 June 2016

Keywords: V doping TiO₂ Optical properties Nano-structured Thin film Resistivity

ABSTRACT

In this research, vanadium doped TiO₂ (VTO) thin film was deposited on glass substrate using sol–gel dip coating method. The structure, morphology, surface roughness, surface composition, optical and electrical properties of the thin films were investigated by X-ray diffraction, field emission scanning electron microscopy, atomic force microscopy, energy-dispersive X-ray spectroscopy, UV-VIS NIR spectrophotometer and MEGGER resistivity meter, respectively. The X-ray diffraction showed that the VTO thin film had a polycrystalline structure. The optical and electrical results indicated that vanadium addition decreased the band gap of the TiO₂ thin film from 3.71 to 3.65 eV and resistivity from $16.7 \times 10^7 \text{ to } 1.7 \times 10^7 \Omega \text{ cm}$.

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1. Introduction

Transparent conductive oxide thin films because of their high conductivity and high transmission in the visible region, play a significant role in various optoelectronic devices such as solar cells, displays, touch screens, light emitting diodes, and etc [1–4].

Most commonly TCO materials are zinc oxide (ZnO), indium tin oxide (ITO), tin oxide (SnO₂), and indium oxide (In_2O_3) [5]. Among them, ITO because of its high conductivity and high transmission in the visible region is most widely used in the optoelectronic systems [6,7]. However, due to scarce resources of indium, high cost and toxicity, its use is limited [7]. ZnO:Al (AZO) and SnO:F (FTO) can replace ITO, because of their non toxic, low cost, electrical conductivity and especially the high transparent in visible region [8–10].

In recent years, TiO_2 has attracted much attention as a TCO materials because of it's high transmittance in the visible and near-infrared region, chemical and thermal stability, low cost and non-toxicity [11–14]. However, TiO_2 has a low conductivity. It is confirmed that doping TiO_2 with metal (Cr, V, Fe,...) and non-metal (N, F, B,...) elements enhanced the electrical conductivity. Some researches indicated that doping TiO_2 with V increased charge carriers and as a result decreased the resistivity [15,16].

In this research, we have prepared V-TiO₂ thin film by a sol-gel method. Then, the optical and electrical properties of V-doped TiO₂ thin films were investigated.

* Corresponding author.

http://dx.doi.org/10.1016/j.ijleo.2016.06.008 0030-4026/© 2016 Elsevier GmbH. All rights reserved.







E-mail address: eshaghi.akbar@gmail.com (A. Eshaghi).



Fig. 1. XRD pattern of the thin films (left) TiO₂ (right) VTO.

 Table 1

 Effect of V doping on the crystallite size, lattice parameter and RMS of the TiO₂ thin film.

V content (w%)	Crystallite size (nm)	Lattice parameter a(A)	Lattice parameter c(A)	c/a Ratio	RMS (nm)
0	13	3.7384	9.1310	2.4424	3.14
1	10	3.7302	9.0044	2.4139	0.78



Fig. 2. FE-SEM images of the thin films (left) TiO₂ (right) VTO.

2. Experimental

To prepare the TiO₂ sol, tetra butyl orthotitanate ($C_{16}H_{36}O_4Ti$) (5 ml, TBOT, 97%) was dissolved in ethanol (50 ml, 99%) and acetyl acetone (0.3 ml, 99.99%). Then, acetic acid (5 ml, 99.7%) and deionized water (5 ml) were added to the first solution and then stirred for one hour. A solution of ammonium metavanadate (NH₄VO₃) was prepared and added as droplet to the above solution under stirring [17]. The content of V was 1 wt%. Before coating, the glass substrates ($25 \times 40 \times 1$ mm) were cleaned with a cotton and ethanol. Thin films were prepared by a dip coating method. The withdrawn speed was 3 mm/s. The gel films were air dried for 18 h, and then heat-treated at 300 °C for 10 min in air atmosphere and then heat-treated at 450 °C for 2 h in air (heating rate; 2 °C/min). The thickness of the films was increased by repeating the above cycles. This cycle was repeated 5 times. The crystal structure of the thin films was evaluated with a Bruker X-ray diffractometer (X'Pert Pro MPD, PANalytical, Cu K α radiation $\lambda = 1.54056$ A). The surface morphology and average thickness of the film was measured by a Field Emission Scanning Electron Microscopy (FE-SEM; Hitachi S4160, Voltage: 30 kV). Surface roughness of the films was measured by an atomic force microscopy (AFM; Dualscop C-26, contact mode). Optical and electrical properties of the thin films were investigated by UV–vis spectrophotometer (Shimadzu UV-T70) and MEGGER resistivity meter (KYORITSU 3126).

3. Result and discussion

The XRD pattern of the thin films is shown in Fig. 1. The XRD pattern shows that thin films have a polycrystalline structure. The thin film has an only anatase phase. Lattice parameters and crystallite sizes of the thin films are calculated and indicated in Table 1. The crystallite size of the thin films is calculated from the strongest peak of $(1 \ 0 \ 1)$ from XRD pattern using Scherer formula [18]. It is observed that the crystallite sizes of the thin films decreased by V doping. In other words, vanadium prevented crystal growth of the TiO₂ and had a substantial effect on it [19]. In addition, No phases of vanadium oxide formed because the V substituted in the titanium position in the TiO₂ crystal structure.

Fig. 2 shows FE-SEM images of the thin films. The VTO thin film is quite homogeneous and there is no peeling or cracks. It may be seen that the average grain size of the TiO_2 thin film decreased by V addition. In other words, doping vanadium prevented grain growth of the TiO_2 [20]. Energy dispersive X-ray (EDX) analysis was used to identify composition of the VTO thin film. The EDX scan spectra of the VTO thin film is illustrated in Fig. 3. The EDX spectrum shows the presence of

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