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Structural and Optical Characterization of TiO_2 Thin Films Prepared by Sol–Gel Process

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Titanium dioxide (TiO_2) thin films were prepared by spin coating technique of sol precursor on Corning 7059 glass substrates. Spectral transmittances of as deposited and annealed samples were measured in the range of 250 to 1100 nm. Optical band gaps were calculated from the Tauc plots and was found to be about 3.78 eV for the annealed samples at 500 °C. X-ray diffraction patterns were performed with as deposited and annealed samples. By annealing the samples at 500 °C in various annealing times, the structure has changed from amorphous to the anatase crystalline state. Variations of the band gap energy values of TiO_2 films with cobalt doping were also investigated. Cobalt doping decreased the band gap value of TiO_2 films down to 3.25 eV. X-ray diffraction patterns were also given for the doped samples.

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1. Introduction

TiO_2 is a large band-gap semiconductor and has a good long-term chemical and photostability [1, 2]. TiO_2 thin films are used in many fields such as catalysis, photocatalysis, dye sensitized solar cells, integrated circuits etc. [3]. They are widely used as photoelectrodes in solar hydrogen production [4] through water splitting. A number of methods have been reported to prepare TiO_2 thin films, including chemical vapor deposition (CVD) [5], spray pyrolysis [6], sputtering [7], sol–gel [8, 9] process, etc.

Titanium dioxide occurs in nature as well-known minerals rutile, anatase, and brookite. They have all the same chemistry but they have different structures. Anatase form is metastable and in many applications shows the best photoactivity. As TiO_2 can only be activated by the UV light of the solar spectrum, for the practical applications, photoactivity of this semiconductor needs to be improved. In order to shift the absorption band from UV to visible region, doping with transition metals is an effective way for improving its photoactivity.

In the preparation technology of new materials, the sol–gel method has attracted special interest. In this paper the preparation of pure and cobalt doped titanium dioxide thin films derived by the sol–gel process are described and the structural and optical properties of the films were studied.

2. Experimental procedure

Titanium dioxide thin films were deposited on Corning 7059 glass substrates by the sol–gel method. 2.5 ml of tetrabutyl titanate (titanium tetrabutanolate) [$Ti(OC_4H_9)_4$] is mixed with 25 ml ethanol (C_2H_5OH) with the purity 99.8% which was used as a solvent and the mixture was stirred at room temperature for 30 min followed by adding of 2.5 ml of acetic acid (CH_3COOH) dropwise into the mixture. They were mixed altogether for 24 h in the magnetic mixer; this solution is transparent and is then mixed with 2.5 ml acetylacetone and 2.5 ml of de-ionized water and is ready for deposition of the films.

For the proper adhesion of the films, cleaning procedure of the substrates is very important. Glass substrates were first cleaned with detergent water for 30 min, then with distilled water for 30 min, 5 min with acetone, 5 min with isopropanol all in ultrasonic cleaner and between every cleaning, substrates were rinsed with distilled water and finally dried with pure nitrogen.

Thin films of $Ti_{1-x}Co_xO_2$ were deposited on Corning 7059 glass substrates using spin coating in 3000 rpm for 20 s and every layer is dried at 500 °C for 15 min and finally annealed at 500 °C in air during 24 h for crystallization. Figure 1 shows the flow chart of the procedure for processing the undoped and Co doped TiO_2 thin films.

The film structures were characterized using X-ray diffraction (XRD) and absorption spectrum measurements. The XRD data of the films were taken using a Panalytical Diffractometer (Philips) with Cu K_α radiation over the range 2θ = 10–70°. The concentration of Co in $Ti_{1-x}Co_xO_2$ films was studied using the energy dispersive X-ray fluorescence (EDXRF) analysis. The X-ray radiation source Mo K_α was used for the excitation of Ti and Co atoms. The Ti and Co concentration in $Ti_{1-x}Co_xO_2$ films were measured by EDXRF intensity of the Ti K_{α_1} and Co K_{α_1} peaks and atomic percent of Co was defined as $x = [Co/(Co + Ti)]$ [10]. The concentrations of Co in $Ti_{1-x}Co_xO_2$ films were varied between

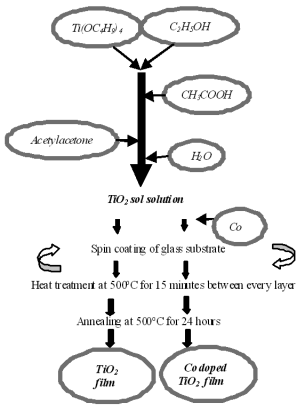

Fig. 1. Preparation procedure of undoped and Co doped titanium dioxide films by the sol–gel process.

$x = 0$ (undoped TiO_2) and 0.244. The transmission spectra of the films were measured in the wavelength range of 250–1100 nm using a Lambda-2 (Perkin-Elmer) (UV--Vis) spectrometer at room temperature. Resistivities of the undoped and doped films were determined by using Keithley 6517A.

3. Results and discussion

Figure 2 shows the XRD spectra of the TiO_2 films, as deposited, after annealing at 500 °C for 24 h, and doping with different Co ratios. As deposited samples are basically amorphous and characteristic peaks are detected corresponding to titania anatase phase after annealing at 500 °C for 24 h. The films are in anatase crystalline state with a preferential orientation of (101). (200) and (211) peaks also appeared in the annealed samples which confirms the anatase crystalline state. Intensity of the diffraction peak (101) decreases and the other two (200) and (211) peaks disappear with the doping by Co ions which reveals the Co ions entering into the structure and substitutes for Ti and crystalline structure distorts more and more with the increase of Co amount in the solution.

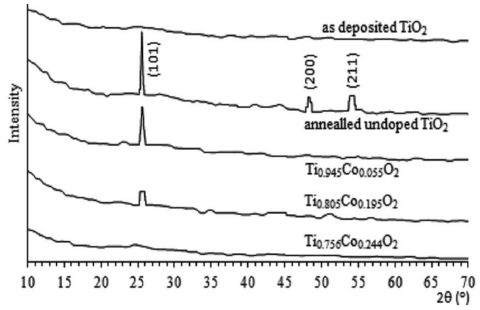

Fig. 2. XRD patterns of anatase TiO_2 films as deposited, annealed and doped.

Estimation of the average grain size in TiO_2 film was carried out using the full width at half maximum (FWHM) values of the (101) peak (Fig. 2) and the Debye–Scherrer formula

$$d = 0.9\lambda/D\cos\theta. \tag{1}$$

Here λ is the wavelength ($\lambda = 1.5405$ Å for Cu K_α), D is the angular line width at half maximum intensity and θ is the Bragg angle. These calculations showed that the average grain sizes of the annealed TiO_2 and Co doped TiO_2 ($Ti_{1-x}Co_xO_2$ for $x = 0.055$) structures were 34.5 nm and 20.7 nm, respectively. Thus the doping of Co (for $x = 0.055$) in the TiO_2 film stimulates the formation of $Ti_{0.945}Co_{0.055}O_2$ with smaller average grain size than that for the TiO_2 film.

Based on XRD data, we determined the lattice constants a and c of annealed TiO_2 sample to be 3.7692 Å and 9.1870 Å, respectively.

Transmission spectra and analysis of the absorption spectra of the TiO_2 and $Ti_{1-x}Co_xO_2$ thin films were shown in Fig. 3a and b, respectively. In Fig. 3a the reflection at the air–film and film–glass interfaces cause the interference in the spectrum. Reports were given by some authors [11, 12] with a detailed study of the absorption edge of anatase TiO_2 prepared by the sol–gel method and a thermal treatment follow a direct type transition. For a direct band gap, the absorption coefficient α is related to light frequency according to the following formula:

$$\alpha^2 = B(h\nu - E_g)/(h\nu)^2. \tag{2}$$

Here E_g is the energy band gap and B is a constant. The resulting plot has a distinct linear regime which denotes the onset of absorption. Thus, extrapolating this linear region to the abscissa yields the energy of the optical band gap of the material.

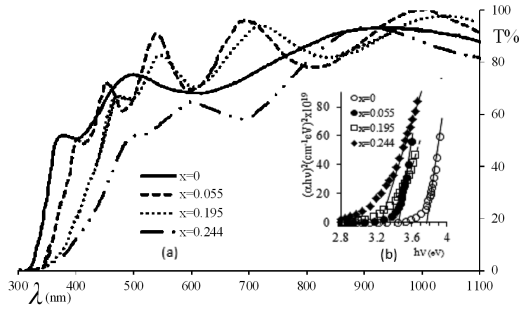

Fig. 3. (a) Transmission spectra for the films, (b) evolution of $(\alpha h\nu)^2$ vs. the photon energy.

The resistivity of the undoped samples were $\rho \cong 4.5 \times 10^9$ Ω cm and is reduced to $\rho \cong 7.1 \times 10^8$ Ω cm for the doped ones. As seen from Table, the band gap energy of direct transition of the undoped ($x = 0$) TiO_2 thin films is calculated to be about 3.78 eV. After Co doping with $x = 0.055$, 0.195, and 0.244, the band gap energy reduced to 3.44 eV, 3.38 eV, 3.25 eV, respectively.

TABLE

Composition parameters and energy band gap values of $Ti_{1-x}Co_xO_2$ structures.

	Composition parameter (x)	Energy band gap [eV]
TiO_2	0	3.78
$Ti_{0.945}Co_{0.055}O_2$	0.055	3.44
$Ti_{0.805}Co_{0.195}O_2$	0.195	3.38
$Ti_{0.756}Co_{0.244}O_2$	0.244	3.25

4. Conclusion

Anatase TiO_2 thin films were successfully deposited by sol–gel spin coating process using tetrabutyl titanate. XRD analysis of the samples shows the conversion of the amorphous form into TiO_2 anatase crystalline phase after annealing at 500 °C. Co substituting for Ti in TiO_2 lattice results in a disorder of the crystal structure. The influence of Co on the band gap energy was also studied. It is clear from the band gap energy results, that with increasing Co concentration the band edge shifts to lower energies. The resistivities of the films were reduced about one order of magnitude by doping with Co. These results suggest that Co doped TiO_2 thin films prepared by sol–gel may be used in photovoltaic applications.

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