Study the structural and optical properties of titanium oxide thin film, doped with chromium prepared in Sol-Gel method

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Abstract

This paper presents the effect of Cr doping on the optical and structural properties of TiO$_2$ films synthesized by sol-gel and deposited by the dip-coating technique. The characteristics of pure and Cr-doped TiO$_2$ were studied by absorption and X-ray diffraction measurement. The spectrum of UV absorption of TiO$_2$ chromium concentrations indicates a red shift; therefore, the energy gap decreases with increased doping. The minimum value of energy gap (2.5 eV) is found at concentration of 4 %. XRD measurements show that the anatase phase is shown for all thin films. Surface morphology measurement by atomic force microscope (AFM) showed that the roughness of thin films decrease with doping and has a minimum value with 4 wt % doping ratio.

Key words

$\text{TiO}_2$ doped, sol-gel, dip-coating.

Introduction

Titanium dioxide (TiO$_2$) has been reported widely recently for its visually interesting characteristics, electronic properties and good stability in natural environments, for high refractive index, wide band gap and chemical stability, polycrystalline TiO$_2$ films for a variety of uses such as optics fabrications [1], dielectric usages [2], dye sensitized solar cell (DSSC) [3], self-cleaning [4], and photocatalytic applications [5]. There are many ways to prepare TiO$_2$ and there thin films [6, 7]. The photo-catalytic properties of TiO$_2$ was first determined by Fujishima and Honda in 1972 [8]. TiO$_2$ can be found as an amorphous layer and also in three crystalline phases: brookite (orthorombic), anatase
(tetragonal), and Rutile (tetragonal). Only the rutile phase is stable thermal dynamics at high temperature. The refractive index at 500 nm relative to the bulk anatase and rutile titanium dioxide are about 2.5 and 2.7 respectively [9]. There are many deposition approaches for preparing TiO$_2$ thin films, such as electron beam evaporation [10], DC magnetron sputtering [5], Sol-gel technique [7], RF reactive magnetron sputtering [3], and plasma enhanced chemical vapor deposition [2]. In this work, Dip-coating method was used to prepare thin films with drawing speed 9 mm/s. The films were deposited on normal microscope slides substrates. Optical, morphological and structural profiles were performed by UV-Vis spectrometer, AFM and XRD techniques.

**Experimental part**

**Pure and TiO$_2$:Cr preparing**

(TiO$_2$) sol was prepared using the following steps: Deionized water was mixed with Titanium tetra isopropoxide or (TTIP) in terms of a molar ratio of Ti: H$_2$O=1:100. To adjust the pH Nitric acid was used and for determining the hydrolysis process of the solution. The solution was set on a magnetic stirrer for (24 hours). The output product (transparent sol) was aged for 6 hours at 55 $^\circ$C. The dopant weight percentage of chromium was (2%, 4%, 6% and 8%) [11].

**Thin film preparing**

Get multi layers of coating (TiO$_2$) by immersing pre-cleaned substrates in solution (TiO$_2$) by dipping method using a dip-coater device. To avoid the sol perturbation, the substrates were stayed in the sol for one minute. After that, it was withdrawn with a fixed withdrawing speed of (9 mm/sec). The substrate was dried in an oven for (15 minutes) at (110 $^\circ$C). Finally, the calcination was done in a furnace for three hours, at (450 $^\circ$C) with a temperature rate of (20 $^\circ$C/min.).

**Results and conclusion**

**UV-VIS absorption**

Optical characterization was achieved by absorption spectra, where the band gap energies were calculated for the prepared samples. Fig.1 shows the absorption of TiO$_2$ doped by metal, in the spectral range (200-800) nm. It is clear that the absorption edge is moving toward red shift as relation to the naked sample in the direction of Cr-doped TiO$_2$.

![Absorption spectra](image)

**Fig. 1: Absorption of pure and Cr-doped TiO$_2$ samples.**
**Band gap energy**

Fig. 2 shows the calculated energy gap value for doped and undoped TiO$_2$ thin films, the energy gap was decreased for all doped thin films and take the least value with sample that doped with 4% wt.

![Fig. 2: Band energy gap for all samples.](image)

**XRD analysis**

X-ray pattern for samples are shown in Fig. 3. This fig shows that, the film was polycrystalline having totally anatase phase. It is observed that the films exhibited characteristic peaks of anatase crystal plane (101), (004), (200), (105) and (211). The nearly sharp peak detected at (25.14) can be related to anatase phase with crystal plane (101), while the intensity of the other peaks is very weak. Crystalline size are illustrated in Table 1.
Fig.3: XRD for pure and Cr-doped TiO$_2$.

| W% | 2θ (degree) | FWHM (degree) | Crystalline size (nm) | hkl | Phase |
|----|-------------|---------------|-----------------------|-----|-------|
| 2% | 25.36       | 0.47          | 32.6                  | (101) | Anatase |
| 4% | 25.19       | 0.74          | 20.8                  | (101) | Anatase |
| 6% | 25.27       | 0.44          | 34.8                  | (101) | Anatase |
| 8% | 25.5        | 0.41          | 37.5                  | (101) | Anatase |

Through Table 1 it is clear that the least crystalline size will be at the concentration 4 % and this is consistent with XRD measurement.

AFM measurements

In order to calculate the surface roughness and morphologies of the samples belong to pure and Cr doped TiO$_2$, atomic force microscopy (AFM) technique has been used. The atomic forces microscopy images (2588 × 2562.87 nm$^2$) of the films prepared on glass substrate at 450°C under air atmosphere are shown in Figs. 4-8.
Fig. 4: Surface roughness and histogram of pure TiO$_2$ sample.

Fig. 5: Surface roughness and histogram of Cr-doped TiO$_2$ (2%) sample.

Fig. 6: Surface roughness and histogram of Cr-doped TiO$_2$ (4%) sample.
nanoparticles can be densely packed in the films with properly uniform surface. Table 2 illustrates the mean average roughness of the surface and root means square roughness Rms, of these films. The surface roughness of films is very small for the films that doped by chrome where, the (Rms) roughness was in range of 0.476 – 1.94 nm. The quite lower at 4% concentration.

| W% | Roughness Rms (nm) | Roughness average (nm) | Height (nm) | Surface area ratio |
|----|-------------------|------------------------|-------------|-------------------|
| 0  | 2.410             | 2.090                  | 8.34        | 2.0200            |
| 2  | 0.532             | 0.461                  | 1.84        | 0.0731            |
| 4  | 0.476             | 0.414                  | 1.63        | 0.0571            |
| 6  | 1.960             | 1.660                  | 4.17        | 0.4950            |
| 8  | 1.940             | 1.640                  | 4.15        | 0.8750            |

The nucleation sites are likely to increase at the case of glass substrates and the atoms have relatively high energy, which results in a decrease in the grain size and the roughness and increase in the uniformity of the surface as mentioned above in the figures. This result agree with Mardare et al. (2000) [12].

**Conclusion**

Pure TiO₂ and Cr- doped TiO₂ nanoparticles were successfully synthesized via Sol-gel technique using
Titanium tetraisopropoxide (TTIP) as a precursor. Cr-doped TiO$_2$ samples were prepared, using Cr(NO$_3$)$_3$ as the dopant sources of Cr. The amount of dopants were varied in four concentrations, 2, 4, 6 and 8 mol%. The obtained products were characterized by several techniques, such as UV-VIS spectroscopy, energy gap, XRD, AFM techniques. By using Sol-gel technique totally anatase phase can be exhibited in the thin film that’s confirmed by XRD measurements. the band gap energies decreased from 3.2 eV (undoped TiO$_2$) to 2.5 eV for 4% of Cr-doped TiO$_2$. This corresponds to the shift of absorption spectrum from near UV into visible region. The results presented by AFM illustrate that the TiO$_2$ thin film surface roughness was decreased after Cr doping.

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