Deposition of Co-doped TiO$_2$ Thin Films by sol-gel method

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Abstract. Cobalt doped TiO$_2$ thin films have been prepared by sol-gel method onto glass substrate at room temperature. In this present work, we are interesting to study the effect of Cobalt doped TiO$_2$ thin films. the concentration of Co was varied from 0 to 6 %at. The obtained films have been annealed at 500°C for 2 hours. X-ray diffraction patterns showed that Co: TiO$_2$ films are polycrystalline with a tetragonal anatase and orthorhombic brookite types structures. The surface morphologies of the TiO$_2$ doped with cobalt thin films were evaluated by Atomic Force Microscopy (AFM). The optical properties were studied by mean of UV–visible and near infrared spectroscopy. The calculated optical band gap decreases from 3.30 to 2.96 eV with increasing Co doping.

1. Introduction

Titanium dioxide, TiO$_2$, can occur in three main crystal structures: anatase, rutile and brookite. The rutile and anatase forms have been intensively studied and have a significant technological relevance, owing, in large measure, to their optical properties: both are transparent in the visible and absorb in the near ultraviolet [1]. In addition, rutile is the most common crystal phase while brookite is scarce. Rutile is then stable high temperature phase (generally in the 600–1855°C), whereas anatase and brookite are metastable and are readily transformed to rutile when heated [2]. Therefore, understanding of the mechanism and the factors affecting phase stability and phase transformation is important. However, all these transformations have remained to this day misunderstood. Therefore, understanding of the mechanism and the factors affecting phase stability and phase transformation is very important for more efficient uses. For instance, metal doping can alter the phase transformation and, consequently, the photocatalytic activity of TiO$_2$. One doping of interest for photocatalysis and other electromagnetic applications is cobalt [3-6]. Indeed, it was reported that the incorporation of metal ions into the titanium crystal lattice can significantly extend the absorption edge into the visible region [7,8] and anatase structure Co-doped TiO$_2$ films, at room temperature, have ferromagnetism (FM)[9,10]. Recently, it was discovered that Co-doped TiO2 thin films may have potential application as diluted magnetic semiconductors (DMS). Among the elaboration techniques of TiO$_2$ thin films, the sol-gel method is emerging as one of the most promising process because it is not only effective in producing thin, transparent, homogeneous, multi-layer oxide components many compositions on various substrates at low cost and allows the choice of the refractive index and thickness of the layer by changing the preparation conditions, but also to easily incorporate and control the cobalt.
In this paper, we report the study of the structural, optical and electrical properties of TiO$_2$ thin films deposited onto glass by sol–gel dip coating technique as a function of the preparation conditions. Structural evolution with annealing temperature and Cobalt concentration are investigated by Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD) and confirmed by Atomic Force Microscopy (AFM) and Scanning Electron Microscope (SEM) images. Transmittance, gap and refractive index of the films are also studied.

2. Experimental

Cobalt doped titanium dioxide (Co:TiO$_2$) films were synthesized on glass substrates by sol–gel technique. The sol–gel solution [11] is performed at room temperature in the following way: 2 cm$^3$ of titanium isopropoxide (Fluka, 99.9) were considered, to which 0.7 cm$^3$ of isopropanol were added drop by drop. The solution was left under closed stirring during 10 minutes. Then, 2.2 cm$^3$ of acetic acid were poured, stirred during 15 minutes. Cobalt (II) acetate tetrahydrate powder was dissolved in methanol and then added to prepare the Co: TiO$_2$ for various at. % of cobalt concentrations Ti$_{1-x}$Co$_x$O$_2$ (x =0.00, 0.02, 0.04, 0.06). Finally, 5.2 cm$^3$ of methanol were added and stirred during 1 hour. The samples were immersed in the sol–gel solution with speed of 12 cm/min, dried at 100°C during 15 min, and finally annealed at 500°C for 2 h. The spectroscopic measurements were performed on Horiba J. Y. Ellipsometer UVISEL. XRD patterns were recorded on Siemens D8 diffractometer using Copper K$_\alpha$ radiation. Optical transmittance was measured on a UV-VIS spectrophotometer. Atomic force microscopy (AFM) was used for the observation of surface morphology for Co: TiO$_2$ films deposited onto glass substrates in a region of 4.68×4.68 µm$^2$. The electrical properties of the layers were determined using the I(V) characteristics by the two probes technique in a coplanar structure with two evaporated gold electrodes. A dip-coating apparatus made in our laboratory was used for the depositions. The substrate was lowered into the coating solution and then withdrawn at a regulated speed of 0.6 cm s$^{-1}$. After each coating, the films were first dried at 100°C for 15 min. The films were then heat-treated at different temperatures ranging between 400 and 500°C with increasing temperature rate of 5°C min$^{-1}$ for 2h in furnace. The electrical properties of the layers were determined using the I(V) characteristics.

3. Results and discussion

3.1 Films structure

Figure 1 shows the XRD spectrums of the thin films of titanium oxide after annealing at 500°C for 0, 2, 4, 6% at of Co and 3 dipping. We observed that the TiO$_2$ thin films with 0 % Co 3 dipping and annealed at 500°C has an amorphose phase while the 2 and 4 % have an anatase phase with plane of (100). For 6% At. Co, we notice the presence of two concurrent phases with three layers, there is a brookite phase. Figure 1 shows the disappearance of Anatase and the appearance of Brookite and the (121) peak intensity increases with increasing concentration of cobalt for 6% At. Co. there is a mixture of two phases and a shifting of peaks to larger angles.

![Figure 1. X-ray diffraction pattern of TiO2 thin films obtained after annealing: at 500°C for 3 dipping and 0, 2, 4 and 6 % At. Co.](image-url)
In Figure 2, we present 2D and 3D AFM images of the TiO2 films prepared on glass substrates corresponding to the annealing temperatures of 500°C for 6%at. Co and two layers. This figure shows the surface morphology and indicates a porous and fine structure with small size grains in anatase phase.

**Figure 2.** 2D and 3D AFM images of the TiO2 films prepared at 500°C for 6%At. Co

### 3.2. Optical properties

Figure 3 shows the TiO2 thin film UV-vis spectra for different Co concentrations, in the wavelength range of 300-900 nm. TiO2 thin films annealed at temperatures from 400 to 500°C represent high transparency coefficients in the visible range of 400-800nm. The Figure 5a shows the transmittance increases with increasing in the Co content and the temperature, at the same time, the threshold absorption moves to the long wavelengths. This can be attributed on the one hand to the structural change and the increase in grain size to increase the values of extinction coefficient K with the rise in temperature (500°C, Figure3).

![Figure 3. Transmission spectra of the TiO2 thin films obtained after three dipping and annealing at 500°C for 0; 2; 4 and 6% at Co](image)

The optical band gaps of films have been estimated from the plot of their absorption coefficient as a function of photon energy and using Tauc formula for direct band gap semiconductors [12]:

...
\[(\alpha h\nu)^2 = B (E_g - h\nu)\].

Were \(\alpha\) is a absorption coefficient, \(B\) is a constant, \(h\) is Planck constant, \(E_g\) is the energy band gap and \(\nu\) is incident photon frequency.

The optical band gap is determinate from the plotting of \((\alpha h\nu)^2\) versus photon energy (eV), the extrapolation intercepting the photon energy axis given the optical band gap \(E_g\). It varied between 3.30 to 2.96 eV at 500°C. According to Figure 4, it is easy to notice that the gap value decreases with increasing temperature treatment. At this stage, we can say that the annealing temperature contributes to the reorganization of the structure and impurities that come to their sites more easily occupied when it rises and the decrease of \(E_g\) can be correlated with the grain size which increases with temperature.

\[\text{Figure 4. Band gap } E_g \text{ of } \text{TiO}_2 \text{ thin films deposited after 3 dipping and annealing at } 500^\circ\text{C for } 0; 2; 4 \text{ and } 6 \% \text{ at. Co.}\]

4. Conclusion:

In this article we have shown that cobalt can be easily incorporated by the sol-gel method. The formation of a phase starts at 350 °C. On aures hand, we verify that the anatase and brookite phases are very unstable. Cobalt can change the absorption edge and the gap of TiO2.

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