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Optical properties of TiO_2 Thin films prepared by Sol Gel method

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Abstract

Titanium dioxide is currently the focus of intensive research because of their interesting chemical, electrical and optical properties. In this work, TiO_2 thin films were prepared by sol gel method, and have been deposited by spin coating technique onto glass substrates (3 – TiO_2/ glass). In this work, we report the effect of the spin speed (2900, 3200 and 4900 rpm) on different optical properties of the films. The samples were characterized by means of Raman spectroscopy, hall measurement and UV-Visible spectrophotometer. The transmission spectra of titanium dioxide thin films indicate that there are two parts, the first is transparent in the visible wavelength spectrum region and the second is opaque in the UV ranges. We found that the transmission curves and the calculated optical band gap increase when thespin speed increases. The Raman spectra have shown the Anatase phase.

Keywords: TiO_2, Thin films, Sol gel, Anatase, Band gap.

1. Introduction:

Titanium dioxide is a white inorganic solid substance,which is thermally stable, non-stable, non-flammable, poorly soluble, cheap non-toxic material that has very good semiconducting properties. Its insensitivity to visible light, because of its band gap of 3.2 eV [1], which enables it to absorb only in the near ultraviolet region, it has high transmittance values of the films in the visible region [2].

It is widely used in vast range of consumer goods and industrial such as treatment of various surfaces, [3]. This generates a significant enthusiasm from scientists for various applications: photocatalytic [4], solar cells [5], gas sensors, anti-reflect coating, and electrochromic systems [6]. Numerous techniques have been used to prepare the TiO_2 thin films including e-beam evaporation [7], chemical vapor deposition [8], sputtering, spray pyrolysis[9], photo-deposition, sol-gel process [10], and hydrothermal method [11]. We have used in this work a method named sol gel process, which is recognized as one of the simplest and most efficient method in terms of quality, simplicity and low cost for the synthesis of thin films materials.

It is known that titanium dioxide has three structural phases which are rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). In nature, rutile is the most common crystal phase while brookite is scarce. Rutile is the stable high temperature phase (generally in the 600–1855°C), whereas anatase and brookite are metastable and are readily transformed to rutile when heated [12].

2. Experimental details:

The coating solution was obtained by dissolving first 1.6 ml of Titanium isopropoxyde ($Ti(OC_3H_7)_4$) from Aldrich 98% was used as TiO_2 precursor [13], in 4.65 ml of isopropanol. The mixture was stirred at 60°C for

10 min. Then 5.15 ml of acetic acid was added and new mixture has been stirred for 15 min. The final mixture was stirred during 2 hours after adding 12 ml of methanol to obtain the sol-gel solution. This solution was spin coated on ordinary glass substrates which were previously cleaned in nitric acid, methanol and acetone at different spin speeds (2900, 3200, 4900 rpm) for 30s followed by a drying process at 100°C during 10 min to evaporate the solvent. And finally the annealing temperature has been elevated to 400°C during 1 hour for growing polycrystalline TiO_2 thin films.

The thickness of the films was estimated between 230,17 and 233,77 nm , the cristallinity of the films was examined by Raman spectrometer, the optical properties of the prepared thin films were examined by a UV-Visible spectrophotometer and the resistivity of the films was measured by the four point probe method.

3. Results and Discussion

a. Analysis of transmission spectra

In Figure 1 we grouped the transmission spectra in the range of 300 to 1000 nm obtained for films prepared at different spin speed (2900, 3200.4900) rpm. These curves show the influence of speed on the optical properties of titanium dioxide thin films. In general, the shape of the spectra is almost identical and these spectra consist essentially of two parts: A region characterized by a strong absorption located at λ <380 nm. So, it is practically in the Ultra Violet field and is mainly due to the electronic inter-band transition, which largely justifies its use in the determination of the optical gap of thin films.

A region of high transmittance; that comprises the visible range, so a wide range of wavelength ranging from 380 to 1000 nm and is in the order of 65% to 90% for all the films. This high transparency is one of the essential characteristics and that fully justify the interest in TiO_2 thin films.

These films are characterized by very near optical spectra. They show that titanium dioxide thin films are transparent in the visible and opaque in the ultraviolet. We also note that the decrease in the speed leads to a small fluctuation band shift towards lower wavelengths. The latter is a consequence due to the nanoparticles increase in number and size.

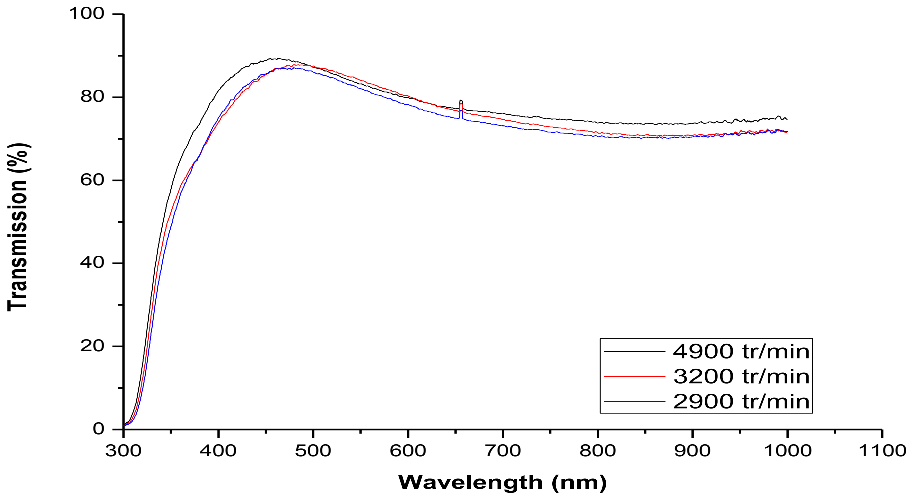

Figure 1: Transmissionspectra of the layers of TiO_2 for various depositions speeds [(2900) rpm, (3200) rpm, (4900) rpm]

i. Calculation of gap Eg

From the curves of transmission versus wavelength determining the absorption coefficient for each wavelength, the variation of $(\alpha h\upsilon)^{1/2}$along with hυ determines the width of the band gap Eg, by using Tauc formation [14]:

$$(\alpha h\upsilon)= B\,(h\upsilon - Eg)^{m} = f\,(h\upsilon)(1)$$

In this formula, B is a constant and m is a coefficient which depends on the type of the authorized transition between the valence band and the conduction band. The values of m are allowed half for an authorized direct transition, 2 for an indirect authorized transition. According to the electronic structure calculations, TiO_2 compound has an indirect gap of 3.2 eV, so m = 2.

From the plot of $(\alpha h\upsilon)^{1/2}$ as a function of hυ, the band gap is obtained by extrapolating the linear part of the curve to the zero (α = 0) absorption as shown in Figure 2.

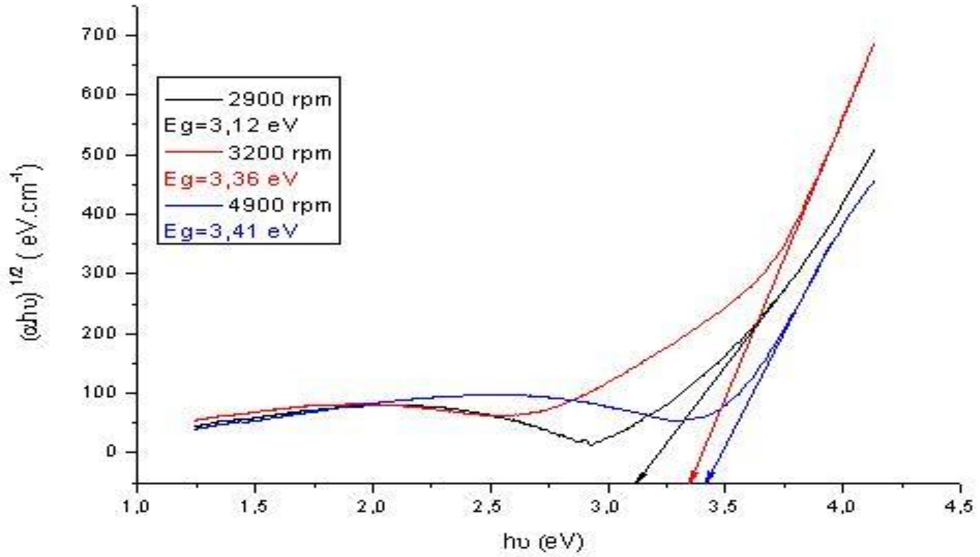

Figure 2: Determination the energy gap by the extrapolation method from the variation of $(\alpha h\upsilon)^{1/2}$ according to hυ for thin layer of TiO_2.

We can see from the Figure.2 that the band gap of TiO_2 thin films increases with the rotational speed from 3.12 to 3.41 eV. This can be explained by the very thin nature of films at high rotational speed, which are more transparent and therefore have a large gap than those at low speeds. These values of band gap are in perfect agreement with those found by others and are very similar to those of the Anatase phase that is 3.2 eV [15].

Table1: Variation of energy gap and film thickness with the change of spin speed

Samples	Eg (eV)	Film thickness (nm)
2900 rpm	**3.12**	**233,77**
3200 rpm	**3.36**	**231,92**
4900 rpm	**3.41**	**230,17**

It is clear that the absorption range of the sample moves to longer wavelengths as well as the rotational speed decreases. The increase of Eg may also be correlated along with the grain size of the material which decreases with the speed.

b. Analysis of Raman spectra

Figure 3 shows the evolution of Raman spectrum of TiO_2 sample at different speeds and annealed at 400 °C for 1 hour. It shows the influence of speed on the training phases. The spectra show a series of vibrational bands identified at 142, 406, 502, and 632 cm^{-1}. These vibrations are due to the presence of the Anatase phase.

c. Analysis of the Electrical properties

Figure 4 shows the variation of resistance of thin films against deposition speeds, the resistance is given by:

$$R_{\square} = \frac{\pi}{ln2}\left(\frac{V}{I}\right)(2)$$

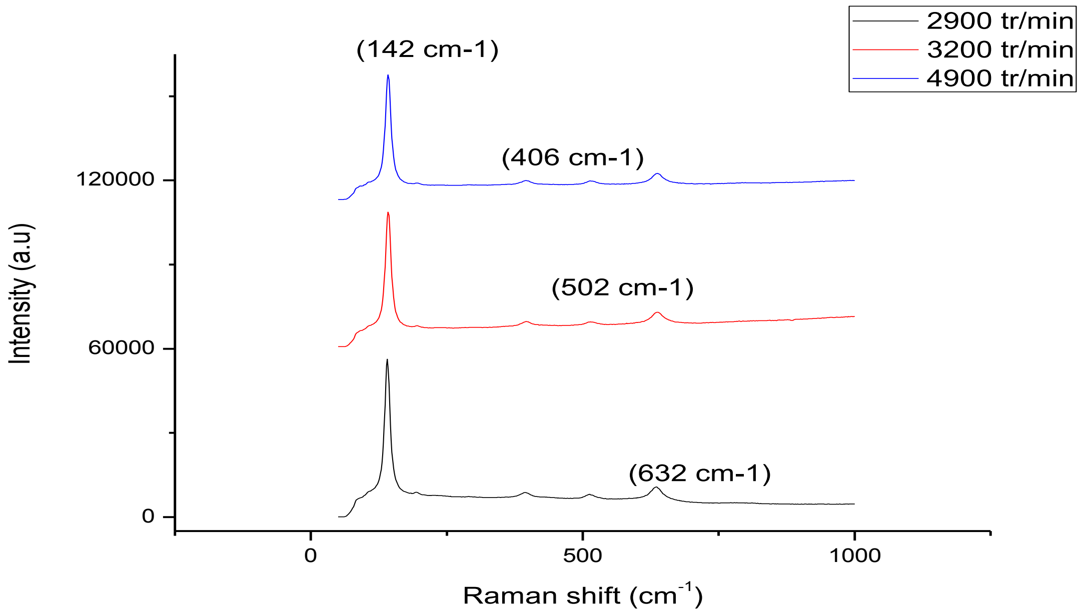

Figure 3: Evolution of Raman spectra of the TiO_2 thin films for different deposition speeds (2900 rpm) (3200 rpm) (4900 rpm)

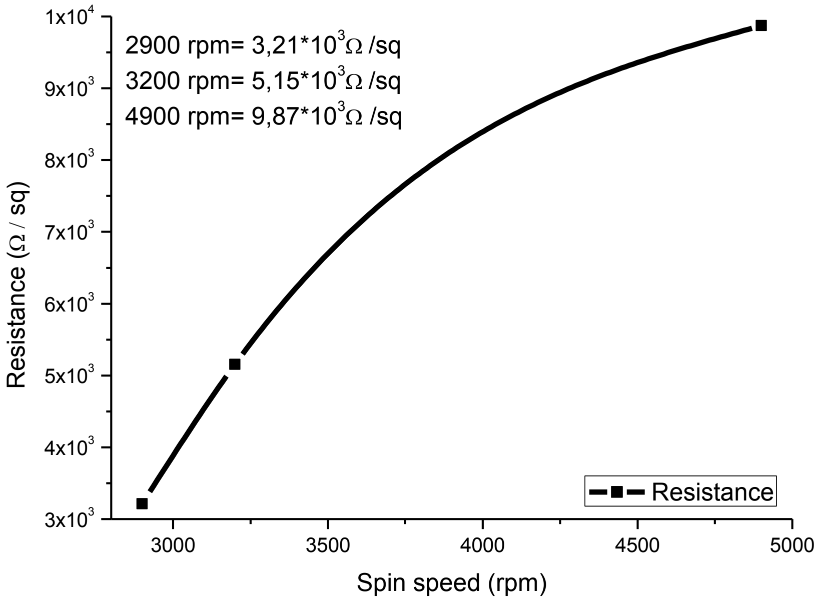

Figure 4: Resistance of the TiO_2 thin films for different deposition speeds (2900 rpm) (3200 rpm) (4900 rpm).

Resistivity of the TiO_2thin films preparedat different deposition speeds and annealed at 400°C are shown in figure 5, the resistivity is given by the following formula.

$$\rho = d\ \frac{\pi}{ln2}\left(\frac{V}{I}\right)(3)$$

Where ρ is the resistivity, d is the thickness of the film in cm.

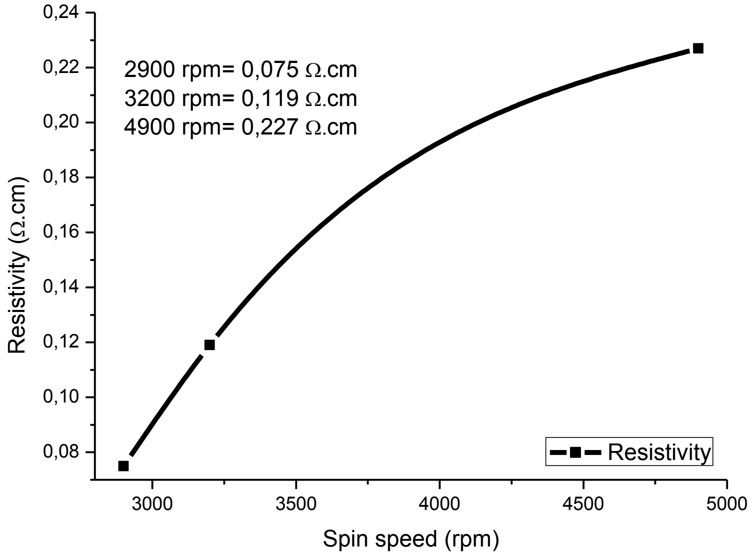

Figure 5: Resistivity of the TiO_2 thin films for different deposition speeds (2900 rpm) (3200 rpm) (4900 rpm).

The resistance and resistivity increase when the spin speed increasing, due to the increasing of spin speed .The electron need to pass through the film with longer time to complete the circuit during the I-V measurement.

Conclusions

The Sol-Gel method that we have adopted for the development of our samples has proved to be a good way to make thin layers of both quality and cost breaking.
The Optical characterization of the thin films shows that the synthesized material is transparent in the visible range, along with an optical transmission varying from 60 to 90%, and in the Ultra Violet is opaque. In the region of high transparency, the transmission decreases with increasing rotational speed. We have also seen that the rotational speed has a significant influence on the band gap of the TiO_2 material.

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