Synthesis and Characterization of Thin TiO2 Films Using the Sol-gel dip Coating Method

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Abstract. TiO2 titanium oxide is a material with many applications, due to its electronic and optical properties, the characterization of the nanostructures developed with this material is carried out in order to determine its physical, chemical, and mechanical properties. This article presents the results of TiO2 multilayered thin film deposited in Corning glass substrate with the immersion technique using the Sol-gel dip coating method. The quality of the film strongly depends on the internal forces of the polymeric chains which lead to viscosity, gravitational force, surface tension, and gravity as an efficient form of obtaining TiO2 thin film. The film was submitted to thermal treatment of 400 °C for 2 hours. The results of the experiment show film with a thickness from 139 to 171 nm that features anatase phase, a crystalline quality that corresponds to the number of deposited layers and have a bandgap close to 3.5 eV. The results show that TiO2 thin film can be used in applications that require high permittivity or high transmittance.

1. Introduction
Titanium oxide (TiO2) has become a very important material for various fields of investigation, due to properties such as chemical structure and mechanical stability, which is important for rust protection combined with photocatalytic attributes with antimicrobial uses. Its low density and thermal stability, biocompatibility, and physical, optical, and electrical properties also make it an attractive material [1]. TiO2 has the ability to be transparent in visible light yet absorb ultraviolet light. Its potential applications in fields such as electrochemistry, water decontamination [2] can be used for solar protection, batteries, and optical coatings in the microelectronic industry and for the destruction of aerial contaminants and the elimination of harmful bacteria, as well as carcinogenic cells. It has also been used in diverse environmental applications for the decomposition of unwanted toxic organic compounds [3]. TiO2 has recently been used for applications such as gas sensors and acidity sensors mainly because of its electrical, morphological, and structural properties, which are of great importance to the crystalline
phase, the size of the grain of crystal, the surface, and if applicable, the type of dopant and its concentration [4]. There are many methods to obtain thin TiO$_2$ film, such as atomic layer deposition (ALD) [5], chemical steam deposit [6], sol-gel [7,8], pyrolysis spray assisted with ultrasound [9], hydrothermal synthesis, and physical deposit methods [10-12]. In general, of all the wet chemical methods, the sol-gel method is most commonly used for the preparation of TiO$_2$, it is considered to be one of the simplest and most affordable for the manufacture of the thin film. The sol-gel method is the evolution of an inorganic network through the formation of colloidal suspension (sol) and the gelation of sol to form a network in the continuous liquid phase (gel). The advantage of sol-gel is that it facilitates obtaining TiO$_2$ crystals of a nanometric size of high purity, offering better control of structure growth. Moreover, the porosity and particle size can be manipulated at atmospheric pressure and at a relatively low temperature [13].

The coating of TiO$_2$ solutions is a liquid depositing process which is obtained using the sol-gel method and generates a complete transformation from sol to gel until it turns into xerogel when the substrate is taken out of the solution bath at a constant speed (U) (see Figure 1). This method produces evaporation and draining of the solution solvent and generates a thin film of TiO$_2$. It is a dynamic and complex depositing process, frequently used due to its benefits and is a simple film creation method that provides good reproducibility [14]. Figure 1 shows the deposit method when the substrate is abstracted from the solution. However, it is complicated to predict the topography of all of the coating area during depositing by means of immersion, since this is completely dependent on time, the agitation of the solution, the induced evaporation of the of the solvent, the precursor concentration, the temperature of the solution during deposits, the viscosity gradients, and the aging of the solution [15]. The pore size of the TiO$_2$ film is controlled with capillary pressure, condensation rates, and the evaporation of the solution. The microstructure of the film depends on the structure of the inorganic species of sol, the adding times, the surface tension of the solvent and the capillary forces when the substrate is taken out of the solution [16]. Finally, the thickness of the film and the uniformity as well strongly depend on the flow conditions when the substrate is in the sol bath, the emersion time, and the evaporation of the solution during emersion.

Figure 1. Draining regimen of Dip-coating method.

2. Methodology
A sol solution was made using 7.4 ml of titanium isopropoxide (IV) (TTIP, 97%, Sigma Aldrich), mixing it with 25 ml of ethanol (99.7%). This precursor was cooled with ice until it reached a temperature close to 4 ºC, after which it was agitated for 5 minutes. The precursory solution was hydrolyzed with the slow addition of a cold mixture which consisted of 0.625 ml of deionized water and 0.04 ml of achlorhydric acid (36.6%) diluted in 25 ml of ethanol. Acid was added as a system catalyzer. The TiO$_2$ sol was magnetically agitated for 8 minutes undercooling. The final sol was transparent and in liquid phase. If the mixture is maintained well shut, it remains stable for at least 3 days.

The TiO$_2$ sol was deposited on commercial corning glass using the dip coating technique, to obtain thin films, an immersion system was used making the deposits at a speed of 2 cm min$^{-1}$, the substrate was kept for 20 seconds inside the sol for the absorption of the liquid. Different thicknesses of the films were obtained depending on the multilayers deposited, which were from one to five immersions. After each
immersion, the films were removed from the system and annealed at 250 °C for 8 minutes. The annealing was performed immediately, ensuring the densification of the sol and avoiding the condensation of the nanoparticles agglomerated by the reagents. Figure 2 shows the methodology for TiO₂ thin film production.

Figure 2. Preparation procedure of TiO₂ thin films synthesis by sol-gel process.

The films were subjected to thermal treatment at 400 °C for 2 hours. The thickness of the film was measured using a Dektak 150 Profilometer, the transmittance and absorbance of the films was measured using a Uv-Vis Evolution 600 Spectrophotometer, the Raman spectra were obtained using Horiba LabRam HR equipment with a 638.8nm helium neon laser (He-Ne).

3. Results and discussion
The film thickness measurement was performed by scanning the surface taking data at the intersection of the substrate and the film every 333 nm over 200 um, Table 1 shows an average of 3 quantifications performed for each film.

| Immersion Numbers (Dippers) | Average Thickness (nm) |
|-----------------------------|------------------------|
| 1                           | 139.23                 |
| 2                           | 146.45                 |
| 3                           | 153.32                 |
| 4                           | 166.17                 |
| 5                           | 171.75                 |

Figure 3 shows the absorbance spectra, the Tauc plot is used to calculate the bandgap (Eg), using the value of the absorption coefficient α given by the Beer-Lambert ratio.

\[
\alpha = 2.303 \log \left( \frac{T}{d} \right)
\]

(1)

where \(d\) is the sample thickness and \(T\) is the transmission. Equation 2 represents the ratio of Tauc as a function of \(hv\) (photon energy), the TiO₂ has an indirect band interval, therefore, \(n = \frac{1}{2}\) is the transition value that has been used. The values of \(Eg\) have been estimated by making an extrapolation of the
absorption slope, acquiring the value of the intersection of this slope with the photon energy when 
\((ahv)^\frac{1}{2}\) is 0.

\((ahv)^n \propto (hv - E_g)\)  \hspace{1cm} (2)

\(h\) is the Planck constant, \(v\) is the photon frequency, \(E_g\) is the bandgap and \(n\) indicates the type of optical transition. It is important to note that the value of the bandgap of the Tauc plot depends on using the appropriate function to match the present electronic transition and the appropriate film thickness [17]. The Tauc plot as \((ahv)^\frac{1}{2}\) versus \(hv\) is represented within Figure 3. The value of \(E_g\) is close to 3.5 eV.

![Figure 3. UV-Visible absorbance and Tauc plot of TiO\(_2\) Films at different thickness](image)

A correlation in the increase in the optical bandgap value and the thickness of the film can be observed. Various factors cause \(E_g\) displacement towards the right. Different studies show that this phenomenon is largely present due to the Burstein-Moss effect, which describes an increase in the bandgap due to an increase in free carrier concentration [18].

![Figure 4. Transmittance spectra of TiO\(_2\) Films.](image)
The transmittance curves of all the film reflect a transmission percentage above 75%, see Fig.4, the spectrums exhibit a perceptible shoulder in the nearby UV region, which is related to the porosity of the film. This property is reduced with an increase in deposited layers.

On the other hand, the first order TiO2 Raman dispersion in anatase phase resides in the D4h (I41/amd), spatial group, and according to group analysis, there are six active vibrational Raman modes, positioned at 144cm⁻¹ (Eg), 197cm⁻¹ (Eg), 399cm⁻¹ (B1g), 513cm⁻¹ (A1g), 519cm⁻¹ (B1g) and 639cm⁻¹ (Eg) [19]. Figure 5 shows the Raman spectrums of the thin TiO2 films, the spectral characteristics obtained experimentally coincide with the reported anatase phase.

![Figure 5. Vibration modes in micro-Raman spectrum of TiO2 Films (a) Raman sprectrum of films D5-D3 (b) Close up to Raman spectrum of films D1 and D2.](image)

The main differences of the spectrum are related to an increase in the amplitude of vibrational modes \(E_g(1), B_{1g}(1), \) and \(E_g(3)\) when increasing the number of film layers, in some cases \(E_g(2)\) is imperceptible. Anatase mode \(B_{1g}(1)\) symbolizes an exclusive vibration of titanium atoms. Peak \(A_{1g}\) indicates that there is a vibration of oxygen atoms, unfortunately, this peak overlaps with mode \(B_{1g}(2)\) and makes it impossible to indicate whether the \(A_{1g} + B_{1g}(2)\) increase is due to possible oxygen vacancies or defects in the titanium-oxygen network of the structure \(E_g(1), E_g(2), B_{1g}(2), \) and \(E_g(3)\) combine vibrational modes of oxygen and titanium atoms [20].

4. Conclusions

Titanium oxide is an attractive material due to its electrical and optical properties, used in many technological applications, including as a sensor film. Thin TiO2 film was synthesized using the sol-gel method and deposited by coating on Corning glass substrates. Deposits from 1 to 5 layers of different thicknesses were obtained, and once the film reached a xerogel state, they were submitted to a thermal treatment of 400º C for 2 hours. The film had transparency higher than 75% in the visible range of the electromagnetic spectrum that can be related to a high preferential orientation or crystallinity. It was possible to obtain optical parameters, surface attributes, and the 3.5eV bandgap interval at the transmittance and absorbance spectrums. The Raman spectrum indicates an anatase phase that increases with the growth of the film, the vibrational modes indicate that the presence of oxygen drives the current leakage lower, which results in higher resistivity. These phenomena suggest that thin titanium dioxide film made with the sol-gel process acts as an insulator with high permittivity. The results suggest that the film can be used as a good insulator with high permittivity dielectric as elements for sensitive devices such as a pH sensor or as a gas sensor for an extended gate transistor, moreover, its use in applications that require high transmittance, such as solar cells, could also be considered. In the future, studies about the characterizations of photoluminescence and DRX will be carried out.
Studies of characterizations of photoluminescence, X-Ray diffraction and hall effect will be conducted in the future.

5. References

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