OPTICAL AND STRUCTURAL PROPERTIES OF TITANIUM OXIDE
THIN FILMS PREPARED BY SOL-GEL METHOD

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TiO₂ thin films were prepared by sol gel method. The structural investigations performed by means of
X-ray diffraction (XRD) technique, Scanning electronic microscopy (SEM) showed the shape structure
at T=600°C. The optical constants of the deposited film were obtained from the analysis of the
Experimental recorded transmittance spectral data over the wavelengths range 200-3000 nm. The values
of some important parameters (refractive index n, dielectric constant ε∞, and thickness d), and the third
order optical nonlinear susceptibility κ(3) of TiO₂ film are determined from these spectra. It has been
found that the dispersion data obey the single oscillator relation of the Wemple-DiDomenico model, from
which the dispersion parameters and high frequency dielectric constant were determined. The
estimation of the corresponding band gap Eg, κ(3) and ε∞ are 2.57 eV, 0.021 × 10⁻¹⁰ esu and 5.20,
respectively

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1. Introduction

Many nanostructured materials are now being investigated for their potential application in
photovoltaic, electro-optical, micromechanical and sensor devices [1]. Nanoporous TiO₂ thin films for dye-
sensitized and ETA solar cells have been under intensive study for many years [2]. TiO₂ occurs naturally as
minerals: rutile, anatase or brookite. The rutile and anatase forms have been intensively studied and have
significant technological usefulness, owing, in large measure, to their optical properties: both are transparent in
the visible and absorb in the near ultraviolet [3]. The rutile (110) surface serves as a prototype model for basic
studies of oxide surfaces, and is the active component in self cleaning cement. It serves as the dye-supporting
electron transporting substrate in a promising class of solar cells. Recent interest has been raised for the
transparent anatase N-doped films [4].

At room temperature the direct gap Eg is 3.06 eV for rutile and about 3.3 eV for anatase. This paper
reports on investigation of optical properties of nanocrystalline TiO₂ anatase films prepared by dip-coating in
the frame of the sol-gel method.

Structural properties, morphology and grain sizes are studied. The substrate is immersed in the solution
four times with speed of 80 mm.min⁻¹. Each layer was dried at 100 °C for 15 min and annealed at 300°C during
30min. After depositing the fourth layer the film was treated at 400 °C for 20 min.

The film structure was determined by (XRD) Cu Kα Dron-3m diffractometer [5]. The UV-Visible
spectra of samples deposited on glass wafer were recorded in the photo-spectrometer FT-IR Perkin -Elmer
SPECTRUM 1000, the surface morphology were analysed by scanning electronic microscopy SEM ESEM XL
30 FEG FEI Company (Philips).The optical study to calculate the refractive index (n), dielectric constant (ε∞)
was carried out for TiO₂ anatase by analyzing the transmission spectra of thin layer (four layers) using the
envelope method proposed by Swanepoel [3]. The optical band gap was calculated by Tauc’s extrapolation
method [6], and compared to the plot of (α hv)² vs hv for the determination of direct band gap Eg.

2. Experimental

The sol-gel solution [8] is prepared in the following way:1.6 cm³ of titanium isopropoxide was
considered, to which 4.65 cm³ of isopropanol are added drop by drop. The solution was left under closed
stirring under heating at 60 °C during 10 minutes. Then 5.15 cm$^3$ of acetic acid was poured, stirred during 15 minutes under heating at 60°C. Finally 12 cm$^3$ of methanol and was added and stirred during 2 hours. The samples were immersed in the sol-gel solution with the speed of 80 mm/min, dried at 100 °C during 15 min, and finally annealed at 400 °C during 20 minutes.

3. Results

Fig. 1, shows the X-ray diffraction (XRD) patterns of TiO$_2$ thin film annealed at 400°C during 20 mn, it is seen that the elaborate TiO$_2$ thin layer has a crystalline structure after annealing under oxygen O$_2$ flux at 400 °C for 20 min, It has been observed two phases, the anatase phase with the preferential orientation of the crystallites along the [101] direction, and the appearance of a very small peak of rutile phase at $2\theta = 47.67^\circ$.

According to Sabataityte and al.[2] who used sol-gel method and spray pyrolysis technics for film deposition, the structure obtained is anatase at 500 °C. On the other hand spin-coating [7] method lead to the formation of the configuration Ti-O-Ti anatase. This modification was observed after an annealing of 450 °C. The rutile crystalline structure was observed after an annealing at temperatures higher than 700 °C.

The surface morphology of the as-prepared TiO$_2$ nanoparticle film, annealed at 600°C for 30 min has been studied by scanning electronic microscopy SEM. It is clearly observed from the micrography that nanoparticles are extra-fine, with an average grain size of 20 nm.

![X-ray diffraction spectra of TiO$_2$ thin layer (four layers) annealed at 400°C during 20 mn](image1)

**Fig. 1. X-ray diffraction spectra of TiO$_2$ thin layer (four layers) annealed at 400°C during 20 mn**

The surface morphology of the as-prepared TiO$_2$ nanoparticle film, annealed at 600°C for 30 min has been studied by scanning electronic microscopy SEM. It is clearly observed from the micrography that nanoparticles are extra-fine, with an average grain size of 20 nm.

![SEM microscopy of the as-prepared TiO$_2$ nanoparticles annealed at 600°C for 30 min.](image2)

**Fig. 2. SEM microscopy of the as-prepared TiO$_2$ nanoparticles annealed at 600°C for 30 min.**
Analysis of optical transmission spectra is one of the most productive tools for understanding of the band structure and energy band gap, $E_g$, of the crystalline structure.

With the aim to study the optical transmission of TiO$_2$ thin film, the dependence of transmittance, $T$, on the wavelength, $\lambda$, in the spectral range 200 nm - 3000 nm, was recorded. Figure 3 shows the transmittance spectra at normal light incidence for as-prepared TiO$_2$ samples before and after calcination at 400 °C for 20 min.

The transmittance of the uncoated glass substrate is greater than 93% over the whole spectral region excepting for wavelengths below 1000 nm where a slight increase of transmission of about 95% is observed, an effect that due to light scattering by bubbles inside the substrate [8]. The transmittance of TiO$_2$ thin film is slightly less than that of the uncoated substrate. Relatively high transmittance of the film is an indication of low surface roughness and good homogeneity [9]. The spectrum can be roughly divided into two regions: a transparent region with the interface pattern and a strong absorption zone in the UV range. In the region of low absorption, the incident light traverses and reflects in film several times and produces the interference fringes. The four observed peaks in the spectra are related to each layer.

From the experimental data of the optical transmittance of the TiO$_2$ thin film, the refractive index has been calculated.

The complex refractive index for the homogeneous film, with uniform thickness, $d$, is defined by the relation $n_c = n - i.k$ [10], where $n$ is the refractive index and $k$ is the extinction coefficient.

The refractive index, $n$[11] has been obtained from the relation (1). In order to evaluate the extinction coefficient $k$ [12] the relation (2) was used.

$$\frac{1}{T_m} - \frac{1}{T_M} = \frac{1}{4} \frac{(n^2 - 1)(n^2 - n_S^2)}{n^2 n_S}$$

$$\text{Fig. 4. Dispersion of } n \text{ and } k \text{ for TiO}_2 \text{ film on glass substrate.}$$
where \( n_s \) is the refractive index of glass substrate, \( T_M \) and \( T_m \) are the maximum and minimum values of the transmittance at the same wavelength, respectively. The spectral dependence of refractive index \( n \), and \( k \) for TiO\(_2\) film is shown in Fig 4.

\[
k = \frac{a\lambda}{4\pi}
\]

\[
\alpha = \frac{Ln \left( \frac{1}{T} \right)}{d}
\]

The absorption coefficient \( \alpha \) have been determined from the spectra using the formula (3), where \( T \) is the transmittance and \( d \) is the thickness of the film. This coefficient is slightly affected by the change of structure at lower energy values. This behavior is probably due to the crystallization process occurring in the films [14].

The thickness has been calculated from the relation [11]

\[
d = \frac{M\lambda_2\lambda_1}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]}
\]

Through the above calculation, \( n \) and \( d \) of the film were obtained. The film thickness \( d \) was found to be about 270 nm, which is in good agreement with the value measured by ellipsometer Jobin-Yvon UVISEL. The value is about 280 nm.

Figure 4 shows the refractive index \( n \) and extinction coefficient \( k \) of TiO\(_2\) film as a function of wavelength. The dispersion curve of refractive index is fairly flat in the long wavelength region and rises rapidly towards shorter wavelengths, showing the typical shape of dispersion curve near an electronic inter band transition. the refractive index is 2.32 at 800 nm near the visible region. The extinction coefficient decreases gradually with the shortening of wavelength. therefore, the calculated \( k \) value actually included the total optical losses caused by both absorption and scattering, this factor is \( 8.9 \times 10^{-2} \) at 800 nm, the low value of extinction coefficient (of the order of \( 10^{-2} \)) in visible and infrared region is a qualitative indication of excellent surface smoothness of the TiO\(_2\) thin film [15].

4. Discussion

Based on the single-oscillator model, wemple- DiDomenico [16] is a semi-empirical dispersion relation for determining the refractive index \( n \) at photon energies \( (h\nu) \) can be written as follows:

\[
n^2(h\nu) - 1 = \frac{E_o E_d}{E_o^2 - (h\nu)^2}
\]

where \( h \) is the Plank constant, \( \nu \) is the frequency, \( E_o \) is the oscillator energy and \( E_d \) is the dispersion energy which is measure of the average strength of inter-band optical transition or the oscillator strength.

**Fig 5.** Plot of \( (n^2 - 1)^{-1} \) against \( (h\nu)^2 \)
By plotting \((n^2 - 1)^{-1}\) against \((h\nu)^2\) and fitting a straight line as shown in Fig (5) \((E_0/E_d)^{-1}\), and the intercept \(E_0/E_d\), on the vertical axis. The oscillator energy, \(E_0\), is related to the optical band gap, \(E_g\) in close approximation by \(E_0 \approx 2E_g\).

Using the curve above the estimated values of the oscillator parameters \(E_o\) is 5.59 eV, \(E_d\) is 23.51 eV, and band gap \(E_g\) is 2.79 eV. It is known that that inter-crystallites boundaries contain structural defects and impurities, these factors having a strong influence on the absorption processes[14]. The value of the refractive index, \(n(0)\), for \((h\nu) \rightarrow 0\), extrapolated from the Wemple-DiDomenico model fitted with the high-frequency dielectric constant \(\varepsilon_\infty = n(0)^2\) [17], is about, respectively, 2.28 and 5.20.

It has been pointed out that the oscillator strength \(E_d\) obeys a simple empirical eq. [18,19]:

\[
E_d = \beta N_c Z_a N_e (eV) \tag{6}
\]

where \(N_c\) is the effective coordination number of the cation nearest-neighbour to the anion \((N_c(TiO_2) = 6)\), \(Z_a\) is the formal valency of the anion \((Z_a(TiO_2) = 2)\), \(N_e\) is the effective number of the valence electrons per anion excluding the cores \((N_e(TiO_2) = 8)\), and \(\beta\) is a constant that depends on the inter-atomic bond \((\beta(TiO_2) = 0.27\) eV). The parameters required to calculate \(E_d\) give 25.92 eV. One can remark that a good agreement between the two calculated values is obtained.

\[
\text{Fig 5. plot of } (\alpha hv)^2 \text{ vs } h\nu \text{ plot for determination of direct gap, } E_g
\]

For photon energy \(h\nu\) falling on the material and assuming direct transitions between the valence band and conduction bands, the absorption coefficient is related to the band gap \(E_g\) in the following manner

\[
(\alpha hv)^2 = C (h\nu - E_g) \tag{6}
\]

where \(C\) is a constant. The \(E_g\) value was estimated to be 2.82 eV by extrapolating the linear part of \((\alpha hv)^2\) vs \(h\nu\) in Fig.5. This value is similar to the value 2.79, found through the equation (3).

According to Wagner et al. [20] the Miller rule is very convenient for visible and non linear and near infrared frequencies, which equalize the third order non linear polarizability parameter, \(\chi^{(3)}\), the so-called non linear optical susceptibility, and the linear optical susceptibility, \(\chi^{(1)}\), through the equation:

\[
\chi^{(3)} = A (\chi^{(1)})^4 = A[E_0 E_d^4/4\pi(E_0^2 - (h\nu)^2)]^4 = A/(4\pi)^4(n^2 - 1)^4 \tag{7}
\]

where the constant is \(A = 1.7 \times 10^{-10}\). The covalency and ionicity of the chemical bonds strongly influence the magnitude of the non-linearity.
Fig 6. The third order optical non linear susceptibility of TiO2 film annealing at 400 °C for 20 mn.

The third order nonlinear susceptibility of TiO2 film is calculated from the equation (7), which is shown in Fig.6. One can see that \( \chi^{(3)} \) increases when the photon energy \( h\nu \) increases. That begins from 0.021\( \times 10^{-10} \) esu. The estimated value of the third order nonlinear susceptibility \( \chi^{(3)} \) using the equation (7) is for \( n(0) = 2.28 \). The limit value is 0.056\( \times 10^{-10} \) esu.

Table 1: The estimated values of the oscillator parameters of TiO2 thin films.

<table>
<thead>
<tr>
<th>Film</th>
<th>T °C</th>
<th>( T_{\text{anneal}} )</th>
<th>Tech</th>
<th>d (nm)</th>
<th>( E_{\text{o}} ) (eV)</th>
<th>( E_{\text{d}} ) (eV)</th>
<th>( E_{\text{g}} ) (eV)</th>
<th>( n(0) )</th>
<th>( \varepsilon_{\infty} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>400°C</td>
<td>20 min</td>
<td>Sol-Gel</td>
<td>270</td>
<td>5.59</td>
<td>23.51 Equation (6) / 25.92</td>
<td>2.79 Extrapolated / 2.82</td>
<td>2.28</td>
<td>5.20</td>
</tr>
<tr>
<td>TiO2 [20]sintered substrate (250°C)</td>
<td>450°C</td>
<td>1h</td>
<td>APCVD</td>
<td>80.4</td>
<td></td>
<td></td>
<td></td>
<td>2.08</td>
<td>3.81</td>
</tr>
</tbody>
</table>

5. Conclusions

TiO2 thin films have been deposited on glass substrate by sol-gel method. X–ray diffraction patterns have shown that the films are non-crystalline. The envelope method was used to calculate their optical constant (n, d) from the transmittance spectra. The dispersion of the refractive index in film follows the single electronic oscillator mode relation. Using this method, the values obtained for the oscillator strength \( E_{\text{d}} \) and the oscillator energy \( E_{\text{o}} \) have been got: 23.51 eV and 5.59 eV respectively. The optical band is estimated to be 2.79 eV compared to 3.2 eV in [4] and the dielectric constant \( \varepsilon_{\infty} \) was estimated to be 5.20. The refractive index was estimated about 2.28, and the thickness was found equal to 270 nm, compared to that measured ellipsometrically, 280 nm. The third order nonlinear susceptibility \( \chi^{(3)} \) has been calculated using Wagner model and the obtained value was 0.021\( \times 10^{-10} \) esu.

References


