# Effect of annealing on the physicochemical and optical properties of the APCVD titanium dioxide thin films for photovoltaic applications


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**Abstract.** In this paper, we studied the influence of thermal annealing on the phase transformation and crystalline structure of the APCVD titanium dioxide thin films, which in turn influence the physicochemical properties and the optical properties of the produced coatings, by means of standard characterization techniques of Fourier Transform Infrared (FTIR) Spectroscopy combined with UV-Vis Reflectance Spectrophotometry. The absorption peaks at 423 $cm^{-1}$ and 610 $cm^{-1}$ which increase in intensity with the rise of annealing temperature, were observed for the produced rutile $TiO_2$ thin films, by FTIR measurements. The absorption peak at 739 $cm^{-1}$ due to the vibration of the Ti-O bonds, was also detected for different annealing temperatures. From UV-Vis Reflectance spectra measurements, the minimum average reflectance of 8.6 % was achieved on the as-deposited $TiO_2$ thin film having an optical band gap of 3.29 eV. The optical band gap of the produced anatase $TiO_2$ thin film was found to decrease from 3.25 eV to 3.20 eV when the annealing temperature increases from 400°C to 500°C. However, it was estimated to be 3.05 eV for the rutile $TiO_2$ film, in good agreement with the FTIR measurements.



## Keywords

Titanium dioxide, annealing, physicochemical properties, APCVD, FTIR, band gap.


## 1. Introduction

Titanium dioxide ($TiO_2$) is one of the most technologically and industrially important optical material, due to its excellent optical transparency [1], wide band gap energy as well as a high refractive index [2], [3] non-toxicity, high thermal stability and high chemical long-term durability providing considerable interest to its use in diverse potential applications such as photovoltaic, photocatalysis, optoelectronics, microelectronics, gas sensor, antireflective coatings, microwave devices,…etc.

$TiO_2$ crystallizes in three crystalline phases: anatase, rutile and brookite. Rutile phase exhibits higher density, higher chemical stability and higher refractive index compared with anatase [4]. However, anatase structure shows a high photoactivity and is mainly used in solar energy conversion and photocatalysis [5].

In this work, a series of anatase and rutile $TiO_2$ thin films were successfully deposited on silicon substrates using an economically viable method of Atmospheric Pressure Chemical Vapor Deposition (APCVD). The Titanium tetrachloride ($TiCl_4$) with high purity (99.9%) was chosen as the most suitable chemical precursor for this application for its apparent advantages as:

- Its low vaporization temperature with a high thermal stability;
- Its capability to generate vapour at low temperature;
- Its low deposition rate which is especially very desirable for thin film applications.

Further interest using this precursor is the growth of rutile structures at relatively low deposition temperatures comparatively with films grown by TTIP (Titanium tetraisopropoxide) precursor. From [6], the $TiO_2$ films grown from $TiCl_4$ proceed with a slower growth rate than those grown from TTIP.

The phase composition combined with the optical band gap of $TiO_2$, are important factors in determining the properties of the produced material and to furnish essential information for the process optimization in order to improve the performance of the films for structural applications with the goal to meet the industrial requirements.

The aim of this work is to study the effects of thermal annealing on the phase transformation and crystalline structure of the APCVD titanium dioxide thin films, which in turn influence the physicochemical properties and the optical properties of the produced coatings.

## 2. Experimental

The $TiO_2$ thin films were prepared in an APCVD reactor using a commercial Titanium tetrachloride $TiCl_4$ as precursor at different deposition temperatures of 450°C and 500°C for a period of 20 min.

A more detailed description of the APCVD process as well as the occurred chemical reactions can be found in our previous article [7]. The deposited $TiO_2$ thin films on silicon substrates were then annealed in air at 400°C and 500°C during 2 hours.

The physicochemical properties of our $TiO_2$ films were characterized by using a “Fourier Transform Infrared (FTIR) Spectroscopy” by means of “Thermo Nicolet NEXUS 670” spectrometer equipped with DTGS KBr detector, in the range of 4000 – 400 $cm^{-1}$ with the resolution of 4 $cm^{-1}$. For comparison, the FTIR measurements were performed in two configurations mode: “Transmission mode” and “Specular Reflectance mode” by means of “Model 500 Variable Angle Specular Reflectance Accessory USRE Manual, p/n 0014-010” equipments at the incidence angle of 45°. For measuring the reflectance spectra of the deposited $TiO_2$ thin films and then extracting the optical band gap, we have used a “VARIAN Cary 500 Model ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometer equipped with an integrating sphere.

## 3. Results and discussion

### *A. Physicochemical characterization of the APCVD titanium dioxide thin films*

The FTIR spectra of our $TiO_2$ thin films, measured in “Transmission mode” are shown in figure 1. This figure reveals the presence of two absorption peaks which are characteristic of the rutile crystalline phase of titanium dioxide, one at 423 $cm^{-1}$ and the other at 610 $cm^{-1}$ for both annealed samples. These absorption peaks were also observed by other researchers [8] for the rutile $TiO_2$ films.

In order to confirm that the intensive absorption peak of 610 $cm^{-1}$ obtained in “Transmission mode” is originate from titanium dioxide (not from silicon substrate); we have performed the FTIR measurements in “Specular Reflectance mode” at the incidence angle of 45°. A further confirmation of this result is illustrated in figure 2.

The absorption peak at 739 $cm^{-1}$ which is seen in the spectra for different annealing temperatures, is due to the vibration of the Ti-O bonds [9].

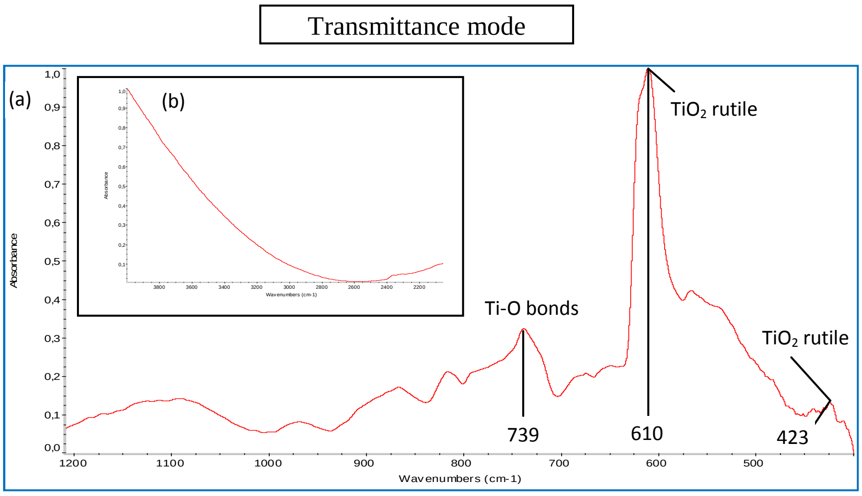
The FTIR signal level of the deposited $TiO_2$ films increases with increasing the annealing temperature from 400°C to 500°C making the difference between the absorption band intensities, but exhibits essentially the same characteristics (Figure 3).

From the FTIR spectra of our samples, no absorption band around 480 $cm^{-1}$ related to the formation of $Ti_2O_3$ [8], was detected. This confirms that no sub-oxides of $Ti_2O_3$ were contained in the films.

Figure 1b shows that no absorption of carbon, organic compounds or absorption of water were occurred in our $TiO_2$ samples by the absence of $CO_2$ characteristic peaks at 2360 $cm^{-1}$ and 2337 $cm^{-1}$ [10] and no detection of OH groups vibrations mode related to the absorption of water, corresponding to 3400 $cm^{-1}$, 3420 $cm^{-1}$ and 3650 $cm^{-1}$ [10], [11], [12].

### *B. UV-Vis Reflectance Spectrophotometry*

In this work, UV-Vis Reflectance Spectrophotometry is employed for measuring the optical band gap from the measurements of the $TiO_2$ films reflectance. Figure 4 shows the UV-Vis reflectance spectra of the as-



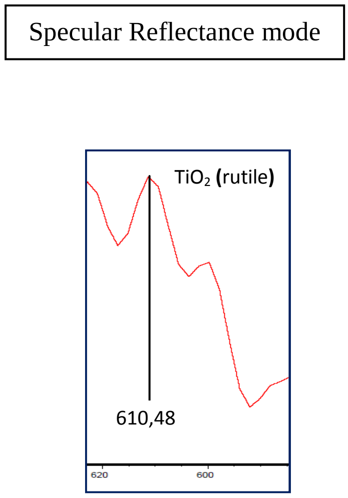




Fig. 1. FTIR spectra of $TiO_2$ thin films deposited by APCVD at 500°C after annealing at 500°C for 2 h: a) over the range of 1200 – 400 $cm^{-1}$ and b) over the range of 4000 – 2000 $cm^{-1}$.

Fig. 2. Zoom on the $TiO_2$ FTIR spectrum over the range of 620 – 580 $cm^{-1}$ in "Specular Reflectance mode".

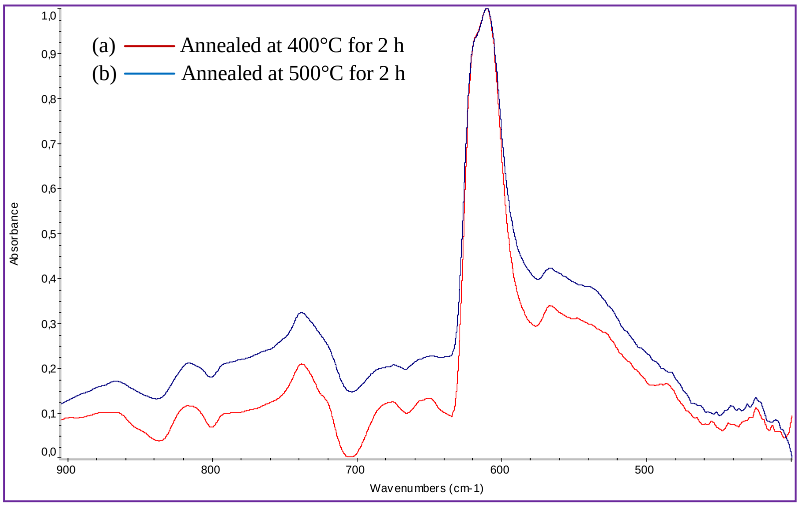



Fig. 3. Comparison on the FTIR spectra of $TiO_2$ thin films deposited by APCVD at 500°C after annealing at:

(a) 400°C for 2 h
(b) 500°C for 2 h.

deposited and annealed $TiO_2$ thin films at different temperatures in the wavelength range from 300 nm to 1150 nm, in which the effect of annealing temperature on the $TiO_2$ samples is very clear when we compare the spectra.

From our experimental results, the minimum average reflectance of 8.61% was achieved on the as-deposited $TiO_2$ thin films (Figure 4a); this value changes with the variation of the film thickness.

With the rise in annealing temperature, we have observed a reduction in the $TiO_2$ layer thickness which causes the respective increase in the film reflectance having a direct effect on the corresponding optical band gap. This process will be explained in detail in the following section.

### *C. Influence of the deposition and annealing temperature on the $TiO_2$ optical band gap*

The optical band gap has been extracted from the reflectance data for each $TiO_2$ sample using the standard formula (1):

$$F(R) = \frac{(1-R)^2}{2R} \qquad (1)$$

$$(F(R) * h\nu)^2 = f(h\nu) \qquad (2)$$

Where R is the reflectance and $\nu$ the frequency.

Then, the optical band gap $E_g$ can be deduced by extrapolation of the linear part of the curve to energy axis as shown in figure 5. Similar curve trends were obtained by [13] utilizing another method.

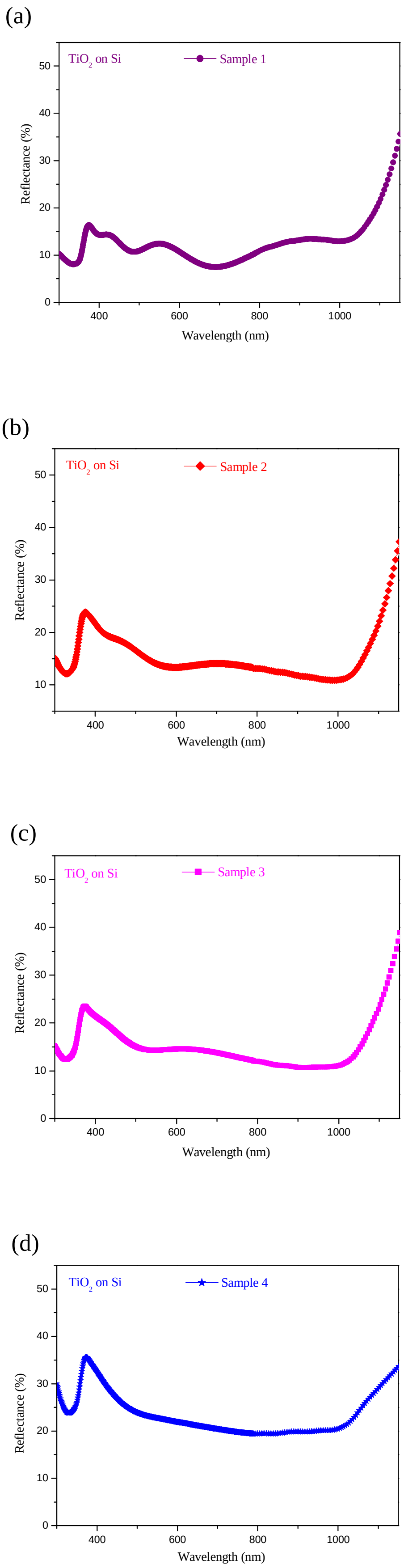



Fig. 4. UV-Vis Reflectance spectra of the APCVD deposited $TiO_2$ thin films: a) as-deposited at 450°C, b) deposited at 450°C and annealed at 400°C for 2h, c) deposited at 450°C and annealed at 500°C for 2 h, d) deposited at 500°C and annealed at 500°C for 2h.

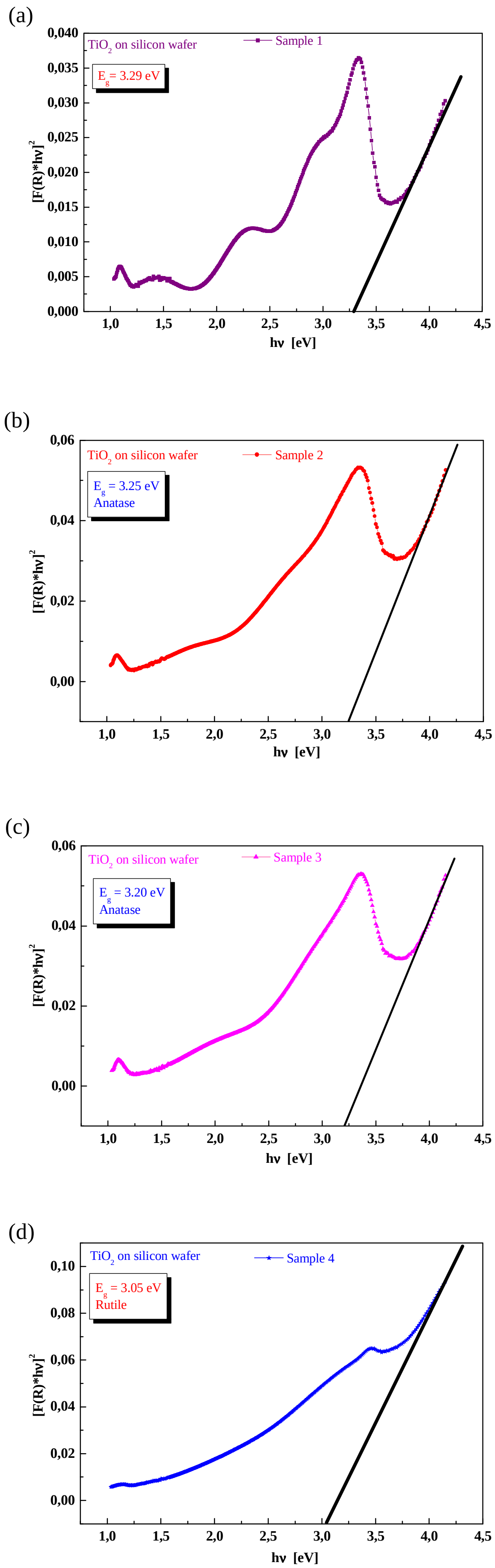



Fig. 5. Variation of the optical energy band gap of the $TiO_2$ films with temperature: a) as-deposited at 450°C, b) deposited at 450°C and annealed at 400°C for 2h, c) deposited at 450°C and annealed at 500°C for 2 h, d) deposited at 500°C and annealed at 500°C for 2h.

As shown in figures 5a, b and c, the as-deposited $TiO_2$ thin films at 450°C lead to an optical band gap of 3.29 eV which was found to decrease after annealing at 400°C and 500°C to 3.25 and 3.20 eV, respectively.

The decrease of the optical band gap with the rise in annealing temperature is attributed to the increase in grain size which varied from 32 nm for the films annealed at 400°C to 39 nm for those annealed at 500°C. The observed increase in crystallite size is due to the crystallization process taking place during the thermal annealing.

The evolution of the optical band gap of our $TiO_2$ thin films agrees with previous studies which report a reduction in the band gap with the increase of crystallinity of the film [14] and particularly support the N.R. Mathews observations [15], who has published a good curve illustrating the decrease in optical band gap with the increase in grain size of the $TiO_2$ films. From [16], the band gap of commercial anatase $TiO_2$ sample with crystallite size of 39 nm, is about 3.2 eV.

At the deposition temperature of 500°C, the optical band gap of the $TiO_2$ films was estimated to be 3.05 eV (Figure 5d) which reflects the rutile phase of $TiO_2$ and agrees with the FTIR measurements (See Section 3.A). This value of band gap is relatively low compared to that estimated for the films deposited at 450°C (Figure 5c). The reason for the observed decrease of the optical band gap with the increase in deposition temperature is due to the phase transformation from anatase to rutile. This can be explained by the increased of densification of the $TiO_2$ films resulting from the rise in deposition temperature. From [4], this densification is accompanied by a decrease in film thickness.

The estimated experimental optical band gaps for our $TiO_2$ films agree with the literature values reported for bulk anatase and rutile structures [17], [18].

## 4. Conclusion

In summary, we can conclude that APCVD technique is an appropriate and viable method for the deposition of thin uniform $TiO_2$ coatings with different crystalline phases: anatase or rutile structures at relatively low deposition temperatures when we use the $TiCl_4$ as the main precursor, especially for photovoltaic applications.

The FTIR studies reveal the presence of absorption peaks at 423 $cm^{-1}$ and 610 $cm^{-1}$ which increase in intensity with the rise in annealing temperature for the produced rutile $TiO_2$ thin films as well as the absorption peak at 739 $cm^{-1}$ due to the vibration of the Ti-O bonds.

The FTIR spectra indicate also that the annealed $TiO_2$ samples were not contaminated by the absorption of water or impurities such as carbon or organic elements.

From UV-Vis Reflectance spectra measurements, the minimum average reflectance of 8.6 % was achieved on the as-deposited $TiO_2$ thin film having an optical band gap of 3.29 eV. The optical band gap of the produced anatase $TiO_2$ thin film was found to decrease from 3.25 eV to 3.20 eV when the annealing temperature increases from 400°C to 500°C. However, it was estimated to be 3.05 eV for the rutile $TiO_2$ film, which is in good agreement with the FTIR measurements.

The phase composition combined with the optical band gap energy of $TiO_2$ films, are vital factors providing essential information for the process optimization in order to improve the performance of the films for structural applications with the goal to meet the industrial requirements.

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