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Effect of the specific surface of Si substrates on photocatalytic activity and optical properties of TiO_2 thin films prepared by sol-gel process

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ABSTRACT

In this paper we report the effect of the specific surface of some substrates on the morphology and optical properties as well as photocatalytic activity of titanium dioxide (TiO_2) thin films prepared using sol-gel method. Used substrates are: Si, textured silicon and nanowires silicon (SiNWs). The surface morphology of the film was examined using Scanning Electron Microscope (SEM). The optical properties of TiO_2 thin films were characterized using UV-VIS, Raman spectroscopy and Ellipsometry. The results showed a remarkable effect of the specific surface of substrates on the morphology and optical properties of TiO_2 thin films.

KEYWORDS

Silicon nanostructure;
TiO_2;
Chemical etching;
Sol gel;
Photocatalytic activity;
Scanning electron microscope (SEM).

INTRODUCTION

Titanium dioxide (TiO_2) is a large band gap semiconductor with many interesting physico-chemical applications in several fields. This dioxide has been obtained in different geometric shape: nanoparticles[1,2], nanowires[3], nanotubes[4,5] and thin films[6] which are generally so expensive. It is worth noting that the methods required for obtained this dioxide is highly expensive, especially if got in various complicated geometric shapes. Besides, the devices made by TiO_2 and silicon nanostructered (Silicon pyramidal and nanowires) material have many short coming limitations in many fields because of the use of costly technical processes. The development of cheaper technical growth of this oxide for optoelectronic applications is then required and thus simple and inexpensive methods, such as the chemical etching technique[7-9], may be used.

During the last decade, the deposition of TiO_2 thin films on various substrates (Si, Si pyramid and SiNWs…) has attracted more attention because of their potential applications in many fields such as: the design of nanometer-scale solar cells and UV- photodiodes. Hence, our study falls within this scope but with a specific focus on the impact of the substrates on the sum of the properties of TiO_2. It is worth noting that heterojunction is obtained with two simple and inexpensive techniques for the static that it is used widely industrially.

This work deals with the preparation of TiO_2 by sol gel deposited on Si, Si pyramid and SiNWs obtained by chemical etching. Using these technical processes, various structures based on TiO_2/substrates have been tested. Here, efforts have been focused on the effect of the specific surfaces on TiO_2 growth mechanism. Also, the photochemical activities of these structures have been carried out in terms of the surface shape.

EXPERIMENTAL METHODS

Fabrication of silicon nanostructures

A p type Si wafer was used as a substrate for the etching of silicon pyramidal and nanowires (SiNWs). The silicon substrates were ultrasonically cleaned successively in ethanol, acetone and isopropanol, for 10 minutes each. The substrates were then immersed in a ($HCl/H_2O/H_2O_2$:1/5/1) solution where H_2O_2 was added to the mixture (HCl/H_2O) heated at 100ºC. Finally, diluted hydrofluoric acid (HF) was used just before rinsing the substrates with ultrapure water.

The etching mechanism of the silicon nanostructed (pyramid and nanowires) is described in figure 1(a and b). First of all, the texture of silicon with random pyramids, are produced by etching in a basic solution. These pyramids are obtained after chemical etching in NaOH (1M) solution heated at 85ºC for 2 minutes. The samples were rinsed with ultrapure water and dried with N_2 gas.

Secondly, the etching mechanism of the silicon nanowires is described in figure 1(b). It is a double step mechanism, in which, as its name indicates, the nanowires growth takes place in two steps: the first is performed in a ($5x10^{-2}$M $AgNO_3$/ HF (10%)) solution for 3 minutes and the second in a (HF(10%)/ H_2O_2(0.6%)) solution for one hour. The obtained samples surfaces are found to be wrapped with a thick silver (Ag) layer that originates from the silver nitrate in the etching solution. To remove completely this Ag layer, the as-prepared samples were treated in a conventional Ag etching solution consisting of (HNO_3(65%)/H_2O) for seconds and then rinsed with ultrapure water.

Deposition of TiO_2 thin film

The heterojunctions were then fabricated by deposed 100 nm thick TiO_2 thin films on SiNWs /Si pyramid and p-Si array by Spin-Coating methods with a speed of 3000 rpm for 30s. A conventional sol-gel method was applied to prepare the TiO_2[10,11]: 4.65 cm^3 of isopropanol was added drop by drop in 1.6 cm^3 of titanium isopropoxide. The solution was left under closed agitation under heating at 60°C for 10 min. Then 5.15 cm^3 of acetic acid was poured stirred for 15 min under heating at 60 °C. Finally, 12 cm^3 of methanol was added and the solution was stirred for 2 h to yield a clear and homogeneous solution, which served as the coating solution after cooling to room temperature. The sol–gel technique offers a low temperature method for synthesizing materials[12]. The sol–gel process has distinct advantages over the other techniques due to excellent compositional control, homogeneity on the molecular level due to the mixing of liquid precursors, and lower crystallization temperature. Moreover, the microstructural properties, i.e. the pore size, pore volume and surface area of the film can be tailored by the control of sol–gel processing variables. Sol–gel preparations are therefore ideal for exploratory studies for large number of materials[13-15].

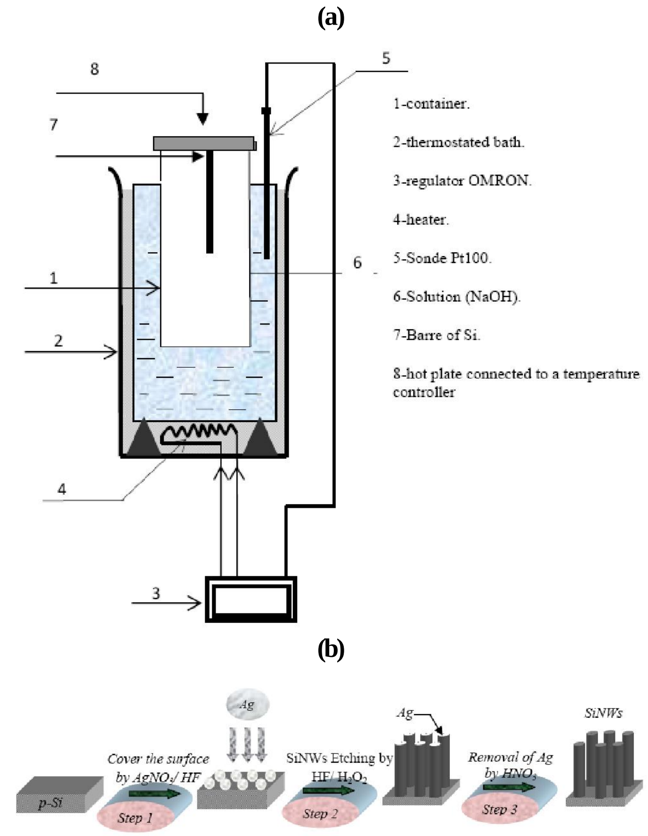

Figure 1 : Silicon nanowires growth mechanism

Characterizations

In order to determine the effect of specific surface of Si substrates on TiO_2 thin film on morphologic and optical properties a scanning electron microscope (SEM) has been used to examine the morphology of the TiO_2/Si, TiO_2/Si pyramid and TiO_2/SiNWs. The Optical reflectivity of the mentioned samples was recorded by means of LAMBDA 950 UV/Vis/NIR spectrometer. On the other hand, the vibrations modes of all samples were investigation by spectroscopy Raman. During this study, the refraction and extinction index of TiO_2 thin films were determined by spectroscopy Ellipsometry.

RESULTS AND DISCUSSIONS

Effect of the specific surface on TiO_2 thin films morphology

Figure 2 shows the SEM images of 100 nm film of TiO_2 deposed on various substrates: Si, Si-pyramidal and SiNWs by sol-gel method. Moreover, the growth of this oxide and its incorporation on SiNWs substrate is then observed at the surface as well as in the bulk, figure 2(c_1 and c_2). In the same line, the incorporation of TiO_2 in such substrate is of the order of 100 nm as shown by the arrow in figure 2-c_2 when compared with figure 2-a_2. This leads to an increase of specific surface of TiO_2 on SiNWs substrate and opens the way to possible future applications of the use of TiO_2 prepared by sol gel method as TCO in photovoltaic solar cells and as on other optoelectronic devices[16-18]. Furthermore, we have so matter what the shape of substrate is TiO_2 takes the same shape of the substrate. This confirms the fact that TiO_2 has a good adhesive with Si substrates.

Spectroscopy UV-visible

The reflectance measurements of the prepared samples were recorded by means a UV/Vis/NIR spectrometer in 300-1200 nm in spectral domain. Figure3 (a and b) shows the reflectance spectra for the bare p-Si wafer, the Si pyramid and SiNWs before and after deposition of TiO_2 thin film. It can be seen that the SiNWs has been dropped to approximately 2 % in comparison to that of the bare p-Si and the Si-pyramid. This remarkably low reflectance is assigned to numerous advantages such as: the high roughness and the geometry of the silicon wires, as well as the collective light scattering interactions among SiNWs array, which trap the light and make it travel many turns over distances much longer than the array thickness[19]. This phenomenon regarding the lower reflectivity of SiNWs remains after the deposition of 100 nm thin films of TiO_2. This result is so encouraging since simple and low cost sol gel and etching techniques has been used to reach so performed devices with low reflectivity phenomenon. These properties can be used for many physical applications such as solar cells, etc.

Raman spectroscopy

Figure 4 shows the Raman spectra in the range of 100–900 cm^{-1} of TiO_2 films deposed on various silicon substrates (silicon (a), silicon pyramid (b) and silicon nanowires (c)) by sol gel method. The (a) and (b) spectra corresponding to TiO_2/silicon and TiO_2/Si pyramid show symmetric vibration modes: $A_{1g} + 2B_{1g} + 3E_g$ of tetragonal anatase phase identified at 140 (E_g), 197 (E_g), 395 (B_{1g}), 433 (B_{1g}), and 640 cm^{-1} (E_g). The band positions are in agreement with previous reports for anatase phase[20]. On the contrary, TiO_2/SiNWs exhibits the presence of others peaks located at 228,436, 619, 676 and 826 cm^{-1} which are assigned to the appearance of no negligible TiO_2 rutile phase. This phenomenon is due probability to the perturbed surface as well as the oxygen presence in such substrate as seen by SEM micrograph, figure 2-c_1.

Spectroscopy ellipsometry investigation

Spectroscopic Ellipsometry measurements were performed at 300 K for wave lengths ranging from 0.2 to 1.4 μm by means of a photometric Ellipsometry with rotating polarizer. Various theoretical models have been used to determine the optical properties of TiO_2 thin films[21-23]. In our case, the experimental results are adjusted to theoretical ones using Forouhi model which describes well the variations of the refractive index and the extinction coefficient of TiO_2 deposited on Si substrate in this wavelength domain as well as around the optical band gap E_g value. This substrate is chosen because it delivers smooth surface in comparison with Si pyramid and SiNWs ones. The Fourier model is used for two sets of sample configurations, figure 5 and the

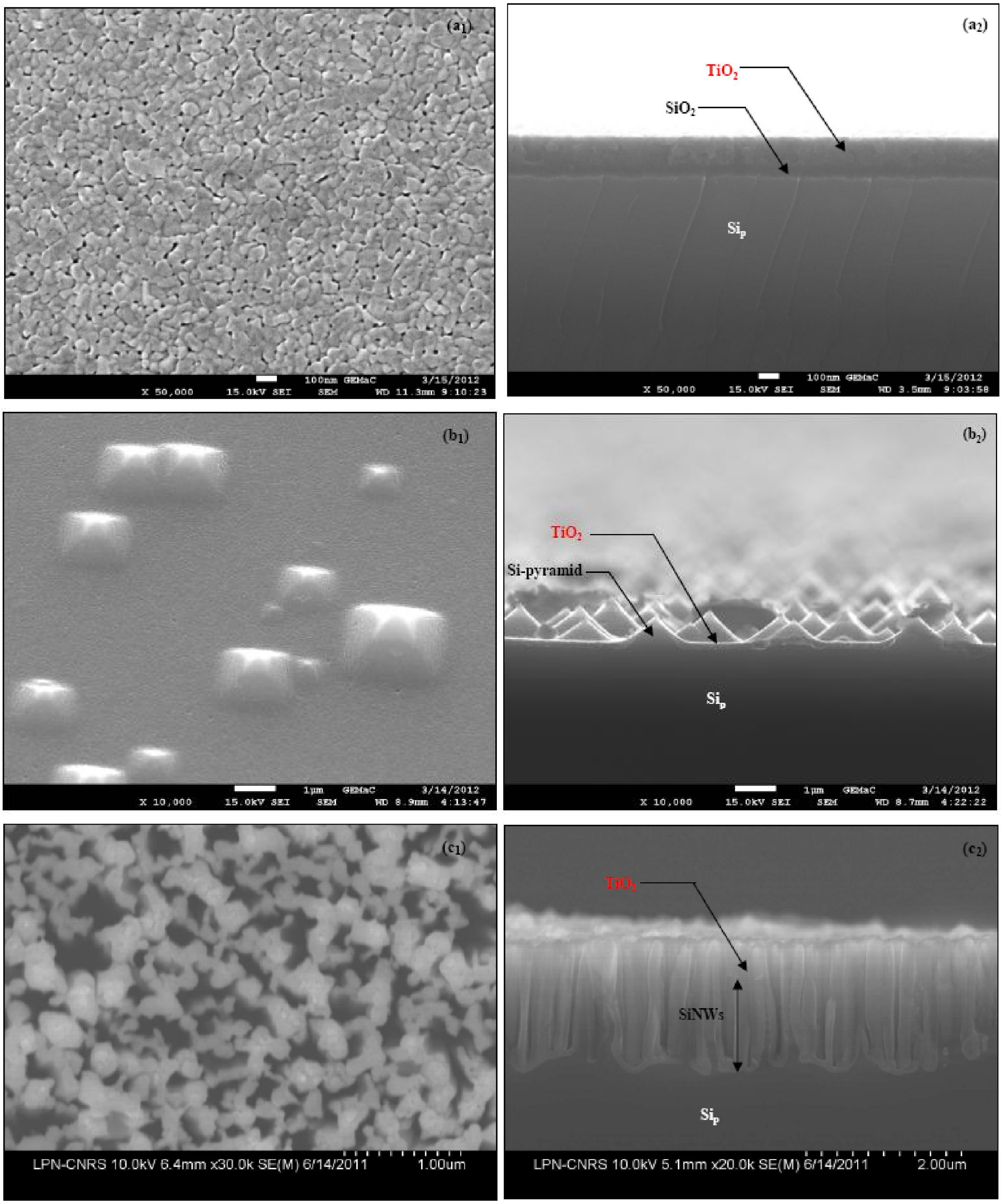

Figure 2 : SEM surface and cross section images of (a_1,a_2) TiO_2/Si_p, (b_1,b_2) TiO_2/Si-pyramid and (c_1,c_2) and TiO_2/SiNWs obtained by chemical etching technique and sol gel method

fitting parameters found by this model are summarized in the TABLE 1.

In the same line, figure 6 exhibits the experimental values of tan (Ψ) and cos (Δ) which were adjusted by

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the calculated curves for both configurations. The model consists of the c-Si substrate with thickness of about 500 μm and can be treated as infinite and two-layers assigned as layer1, layer 2, with respective thicknesses e_1 and e_2. The layer 1 is SiO_2, this oxide layer is due to oxidation of substrate, while the layer 2 is best modeled by the Forouhi and Bloomer dispersion law.

The same figure depicts a good agreement between experimental and calculated curves of tan (*Ψ*) and *cos(Δ)* in the spectral range varying from 0.2 μm to 1.4 μm. This agreement confirms the choice of Forouhi formalism as a theoretical model for the study of optical properties of TiO_2 thin films by Ellipsometry[24].

Figure 7 shows the changes of refractive index (n) and extinction coefficient (k) of TiO_2 thin films in the wavelength range 0.2–1.4 μm, derived from model fitting from the experimental spectroscopic Ellipsometry data is shown in figure 6 (a and b). The calculated thickness and porosity of TiO_2 thin layers are about 97 nm and 13% respectively achieved by adjusting the theoretical values to the experimental results. This value regarding the thickness matches the one given by SEM cross section view, figure 2-a_2. On the other hand, when the wavelength value increases, the refractive index increases until λ take 780 nm, and then become nearly constant with decreasing photon energy. The decrease of light occurs at λ equal to 377 nm, close to the energy gap value.

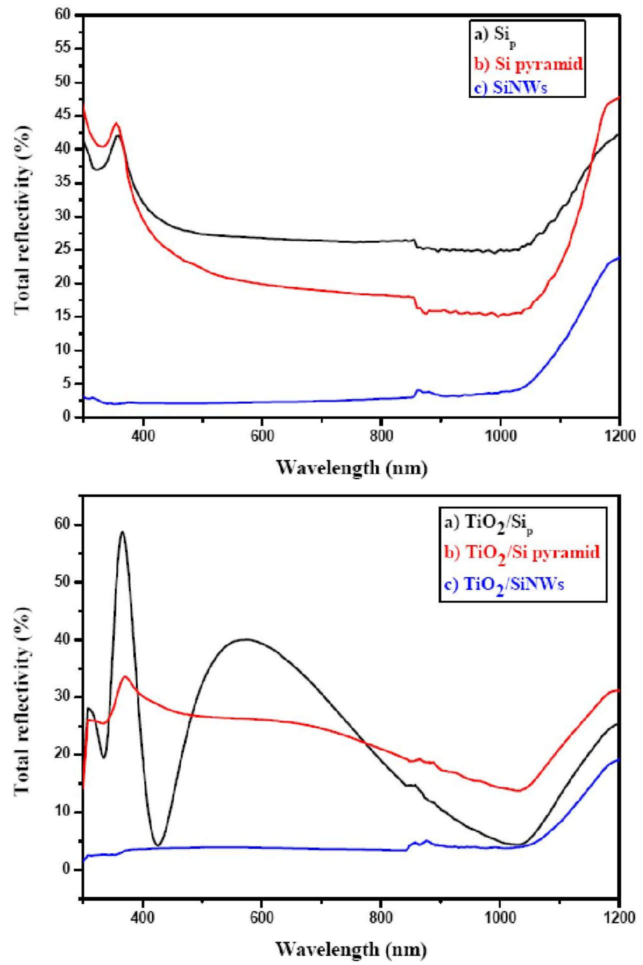

Figure 3 : Dependence of the total reflectivity of (a) Si-pyramid and (c) SiNWs before and after depot of TiO_2 thin films. The reference corresponds to the bare substrate

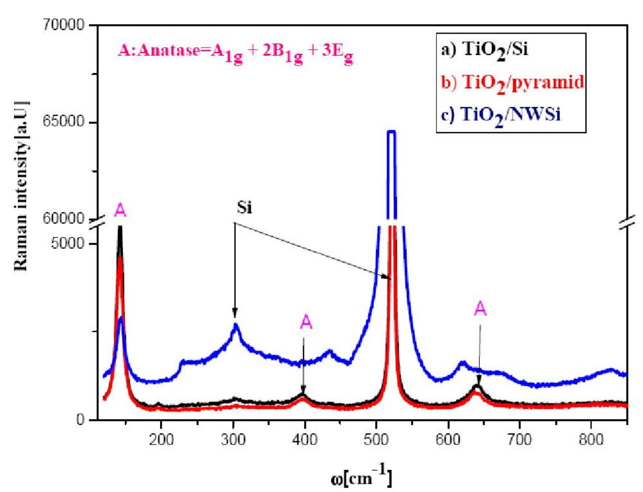

Figure 4 : Raman spectra of the (a) TiO_2/Si_p, (b) TiO_2/Si-pyramid and (c) TiO_2/SiNWs

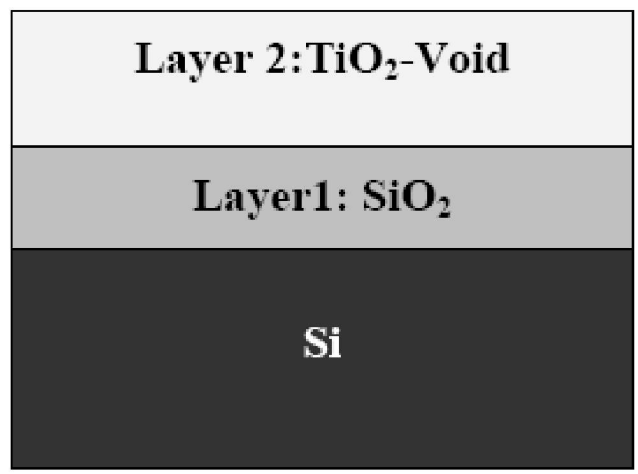

Figure 5 : The multilayer model of the TiO_2 thin film on Si Substrate prepared by sol-gel method

Photocatalytic degradation of methylene blue (MB) by TiO_2/Si, TiO_2/Si pyramid and TiO_2/SiNWs

Among various applications and possible roles which can be played by this specific surface of TiO_2 is the use of this oxide as a catalytic agent. Water pollu-

TABLE 1 : Accurate fitting parameters of the Forouhi model to adjust the theoretical parameters to determine the refraction index and extinction coefficient of TiO_2 thin films

	Thickness (nm)	Void volume fraction	E_g (eV)	N_∞	P_1 Peak			P_2 Peak		
					A	B	C	E	F	G
Layer 2	97	20%	3.25	2.14	0.1118	8.2528	17.1930	0.0003	1.8272	0.8360
Layer 1	20	-	-	-		-			-	

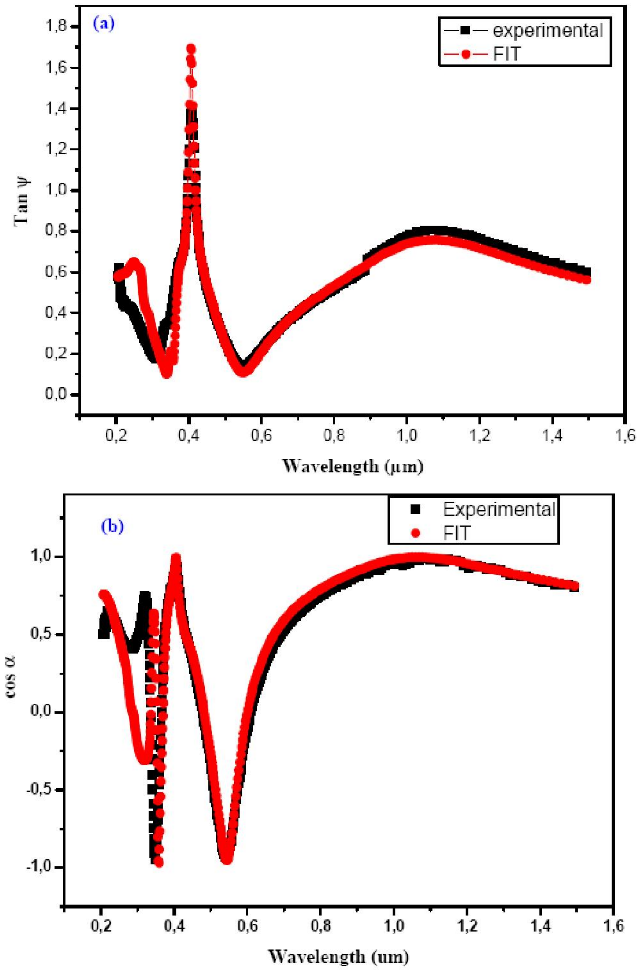

Figure 6 : Ellispometric measurement (Scatters) and modelling (lines), in terms of (a) tanψ and (b) cosΔ, as a function of wavelength, for TiO_2 annealed at 800°C in air for 1 h

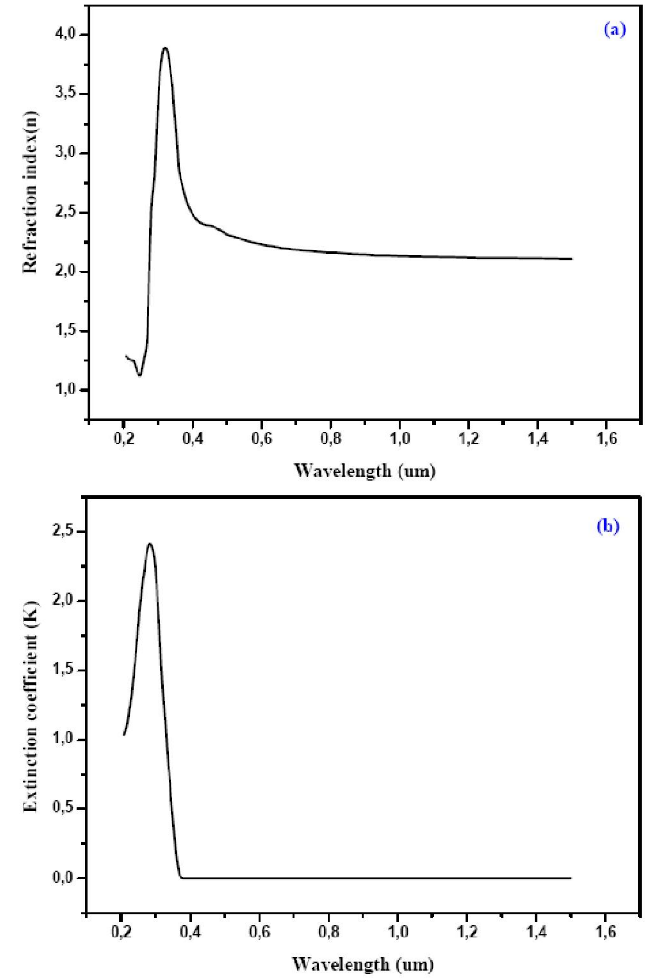

Figure 7 : Refractive index (a) and extinction coefficient (b) as a function of wavelength of Titanium dioxide (TiO_2) anatase phase

tion due to the release of chemicals from industrial sectors (aliphatic and aromatic detergents, degreasing agents, volatile organics, and chlorophenols) has been was a major concern in recent years. Although several semiconductors such as ZnO, Fe_2O_3 and CdS have been used, TiO_2 has been the photocatalyse of choice due to its photostability, non-toxicity, red-ox efficiency and availability since the photocatalytic activity of TiO_2 is influenced by the crystal size, crystal structure, crystallinity, and surface hydroxylation. Herein, we present recent advances we have made on this oxide deposited by sol-gel technique on different substrates (Si-bare, Si-Pyramids and SiNWs) using Methylene blue (MB). The photodegradation of MB in an aqueous solution has occurred under ultraviolet light irradiation for 1 h. The UV light was obtained using a lamp (Northen Electronic. Wigan. Lancs), figure 8. It is noted that during the test only one side of 2 x 2 cm^2 area is dipped in 10 ml of aqueous solution of MB (0.1 M). Also, in the same experiment, the distance between the solution and

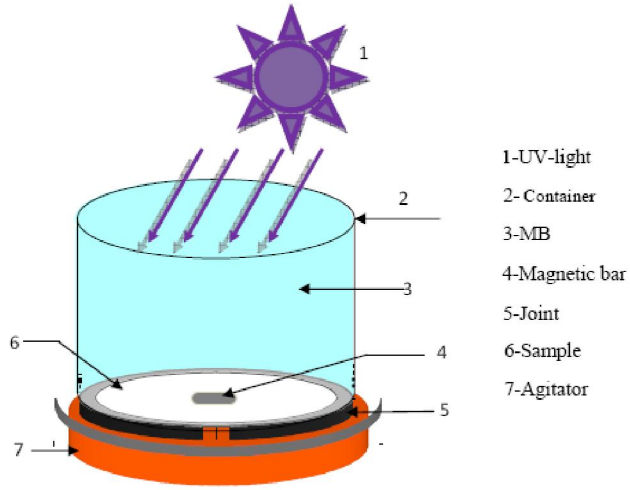

Figure 8 : Experiment setup of photocatalytic activity

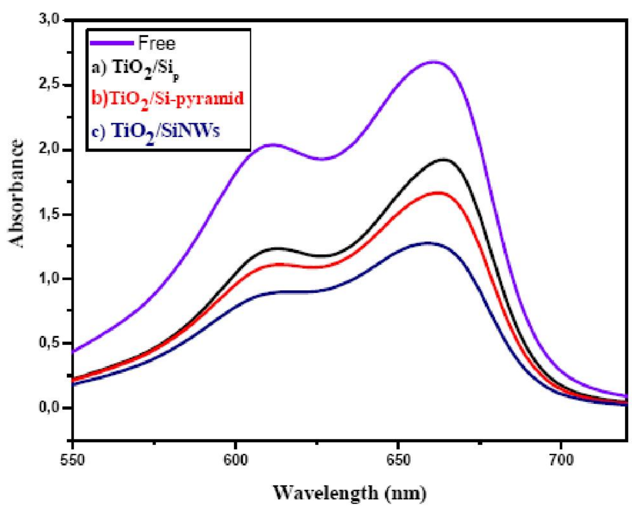

Figure 9 : Variation of the dye absorption spectra using TiO_2 thin films deposited by sol-gel on various substrates on the photocatalytic activity

Lamp (U-V) was 20 cm from the top surface of the solution. Figure 9 shows a significant decrease of the photocatalytic activity in terms of the increase of the specific surface.

It is interesting to note that previous studies had already reported the photocatalytic activities of various TiO_2 powders using several types of commercial anatase and few types of rutile, and concluded that the anatase activity of the auto oxidation is much higher than that of rutile. Here, the mixture between the two phases gives a noticeable photocatalytic activity of TiO_2 thin films grown by sol gel process on SiNWs which may be due to the effect of the specific surface. This result seems to be the main idea provided by the present work.

CONCLUSION

TiO_2 thin films have been prepared by sol gel method. Some physical investigations have been carried out to reach the morphology and optical properties of such oxide films. The use of the deposition of TiO_2 on various substrates (Si, Si pyramidal and SiNWs) shows the importance of the specific surface parameters on the photocatalytic activity. This phenomenon could be improved by an appropriate doping of TiO_2 thin film. Further investigations are in progress to use these results for the preparation of other optoelectronic devices.

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