Photoconductivity Study of TiO_2 Thin Films Annealed in Oxygen Ambient

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***Abstract* - The TiO_2 thin films have been prepared on microscope glass substrate using sol-gel dip coating method annealed at different oxygen flow rate from 0 to 2.3 l/min. The thin films were characterized using Current–Voltage (I–V) measurement, UV–Vis-NIR spectrophotometer and SEM. UV–Vis-NIR spectra reveals all films exhibit high transmission (>60%) in UV-NIR region. From I-V measurement result, the electrical properties were studied in dark and under illumination as a function of oxygen flow rate. Introduction of oxygen in TiO_2 based coatings induces an increase of their electrical resistivity. The reduction of TiO_2 thin film's hardness with increase of the oxygen flow rate is discussed based on film structure that shown by SEM.**

Keyword - TiO_2 ,Sol gel Dip Coating Method, I–V measurement, UV–Vis-NIR spectrophotometer, SEM.

I. INTRODUCTION

Titanium dioxide (TiO2) has many excellent physical properties such as a high dielectric constant, strong mechanical and chemical stability, and low electrical conductivity. Due to its high reflective index and optical transmittance in the visible range, TiO2 is especially suitable as a material for optical coatings and protective layers for very large-scale integrated circuits [1].

Titanium dioxide has attracted much attention during the past years in view of its many applications. Films of this porous nanocrystalline material have been proven to be the most suitable for sensors, optical devices, photoelectrochemical solar cell, as well as for photocatalysis of water, organics and bacteria. Taking into account its chemical inertness, photostability, nontoxicity and low cost, TiO_2 is considered as one of the most promising materials. Thin film of titania can be obtained by various methods such as spray pyrolysis, colloidal suspension and sol gel procedure [2,3]. In comparison with other methods the sol–gel method has some advantages such as controllability, reliability, reproducibility and can be selected for preparation of nanostructured thin films [4,5]. Chemical compositions, structural and optical losses of the films depend on film preparation conditions.

Sol–gel coating has been classified as two different methods which are named as dip and spin coating. The dip coating has considerably been used for preparation TiO_2 nanostructured thin films [5,6,7] .The size of nanocrystals depends on the temperature of annealing. In the nanocrystalline porous TiO2 the oxygen adsorption has a great influence on photoconductivity [8,9]. In the present study we attempt to use the sol-gel method to prepare TiO2 photoconductive films.TiO_2 has three phase in nature, brookite, anatase and rutile. It is amorphous for deposition temperature up to 300^{o}C, anatase and rutile at typically ~350^{o}C and ~800^{o}C, respectively [10].

The oxygen vacancies are intrinsic for any oxide material and act as electron donors, determining the TiO_2 n-type conductivity. Surface hyroxylated Ti sites act as traps [11] for electrons through oxygen molecules, when adsorbed, tend to capture electrons.

II. EXPERIMENTAL DETAILS

A. *Preparation of TiO2 samples*

All the obtained thin TiO2 films were prepared by sol-gel, dip coating technique. Titanium (IV) Butoxide (TTIB) was used as the Titanium precursor. The quantity of 6.8ml of TTIB was dissolved in 50ml of ethanol in a closed beaker at room temperature, with vigorous stirring. After that, 5ml of Acetic Acid, Glacial (GAA) and one drop of Triton X-100 was added into the solution. Then, 0.36ml of deionized water was added and the solution of refluxed under dry atmosphere with stirring for 1 hour at 60^{o}C. After 1 hour, the solution was stirring for 1 hour without heating. The result was a transparent solution.

The glass microscope slide was dipped in the above solution and then drawn up at a withdrawal speed of 1mm/s. First coating was deposited and the resulting gel films were fire for 10 minutes at 150^{o}C and left to cool down slowly. Five group of samples consisted of five layer TiO_2 film were obtained by repeating the dip coating and thermal treatment procedures. Those samples were annealed at different oxygen flow rate at 500^{o}C (Refer table 1).

B. *Characterization techniques*

For the electrical characterization, the electrical resistivity of TiO2 films was measured at room temperature. In order to measure the resistivity, coplanar gold electrodes were vacuum deposited where the electrodes length 0.1mm and the distance between them 3mm. The light was switched on and off to indicate the photocurrent response during illumination and in dark. The conductivity was obtained base on resistivity curve.

The optical properties were calculated from ultraviolet-visible spectroscopy (UV-Vis) absorbance spectra. Ultraviolet-visible spectrophotometry refers to absorption spectroscopy in the UV-visible spectral region. This means it uses light in the visible and adjacent near-UV and near-infrared (NIR) ranges. Spectroscopic analyses of TiO2 films were performed by using a UV–visible spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I / I_o are called the transmittance, and are usually expressed as a percentage (%T). The absorbance, *A (equation 1)*, is based on the transmittance [12] .

$$A = -\log(\%T / 100\%) \qquad (1)$$

The optical transmittance and absorption spectra were recorded in the wavelength range of 200–800 nm. The surface morphology of TiO2 films was characterized with scanning electron microscopy (SEM) and the thickness measurements were performed using surface profiler. The total thickness of five films was found approximately 150 nm.

III. RESULTS AND DISCUSSION

Table 1. The measured samples with their different oxygen flow rate and annealing temperature.

Samples	**Oxygen flow rate(*l*/*min*)**	**Annealing Temperature (^{o}C)**
1	0	500
2	0.9	500
3	1.3	500
4	1.5	500
5	2.3	500

A. *Electrical Characterization*

The resistivity of TiO_2 thin film was obtained by implement the values current and voltage (equation 2) to the (equation 3). The resistivity of TiO_2 thin films is proportional to the value of resistance (Equation 3).

$$V = IR \qquad (2)$$

$$\rho = \frac{RA}{L} \qquad (3)$$

Where:

ρ : resistivity

R: Resistance

A: Thickness of thin film x Length of Au

L: Distance between Au electrodes.

1) Resistivity

Figure 1 shows the electrical properties of TiO_2 thin films prepared as a function of varying the oxygen gas flow rate. The resistivity of TiO2 thin films decrease rapidly between an oxygen gas flow rate of 0 and 1.3 *l*/min. As expected, the resistivity decrease with oxygen flow under both dark and light conditions. The decrease in resistivity with oxygen flow can be explained as follows: the grain size increase with oxygen flow which leads to a decrease in grain boundaries and hence resistivity [13].

When above the oxygen flow rate of 1.5 *l*/min, the resistivity of TiO_2 thin films increased because the oxygen vacancies in the TiO_2 thin films were substituted by oxygen atoms and the additional oxygen atoms in the TiO_2 thin films function as carrier traps [14]. This high resistivity can be due to the high band gap of material.

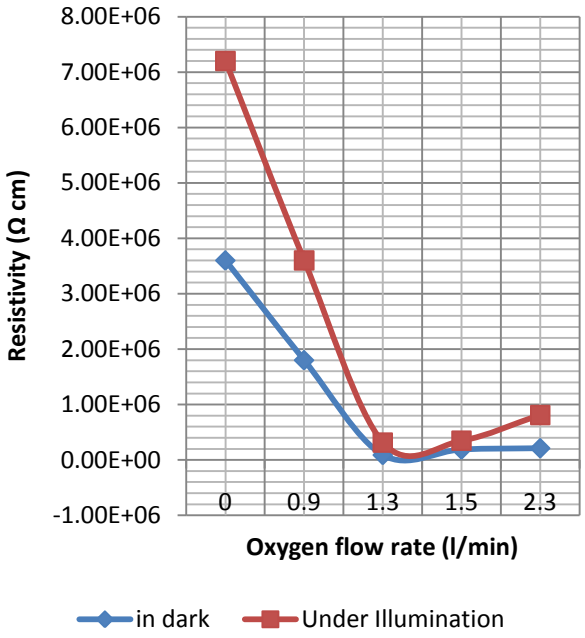

Figure 1: Resistivity vs Oxygen flow rate.

2) Dark conductivity

TiO_2 is well known as n-type semiconductor and its electrical properties are determined by donor-like oxygen vacancies and extrinsic impurities. In this work we study the electrical conductivity in dark of five groups of samples (sample 1 as reference) that annealed at different oxygen flow rate [15].Since in air the most reactive gas is oxygen, the exposure of the samples to air result in the absorption of oxygen molecules, O_2 , at the surface [16].

The measured dark conductivity (σ_d) of the studied samples at oxygen flow rate of heated treated at 500°C and oxygen flow rate as in table 1 gives the results $2.22x10^{-7}$, $7.11x10^{-7}$, $3.5x10^{-6}$, $1.2x10^{-6}$, $6.67x10^{-7}$ for the sample 1,2,3,4 and 5 respectively.

3) Photoconductivity

It is known that during illumination the photogenerated holes are trapped at the surface of TiO_2 [17]. Taking into account that TiO_2 hole mobility is very low and that electrons have much higher mobilities [18], it can be assume that the electrons are the dominant carrier species. The measured photoconductivity (σ_p) of the studied samples at oxygen flow rate heated treated at 500°C and oxygen flow rate as in table 1 gives the results $3.17x10^{-7}$, $8.33x10^{-7}$, $3.61x10^{-6}$, $1.11x10^{-6}$, $6.35x10^{-7}$ for the sample 1,2,3,4 and 5 respectively.

Figure 2 shows the plot of electrical conductivity (σ) of TiO_2 thin films at different oxygen flow rate. The relationship between conductivity and resistivity is written in equation below (equation 4 and equation 5). It shows that, conductivity in dark was lower than in illumination condition. The conductivity of TiO2 thin films increase rapidly between an oxygen gas flow rate of 0 and 1.3 *l*/min. A high decrease of the electron-trapping rate dominates, as photogenerated electrons gradually fill electron traps, resulting in a quick rise of the photoconductivity [19]. It reaches maximum point when most of the trap full. Then, it decreases rapidly between an oxygen gas flow rate of 1.3 and 2.3 *l*/min. The decrease of the photoconductivity amplitude can attributed to the enhancement of the recombination rate by the released electron from the traps to the conduction band [20]. The higher value of conductivity when oxygen flow at 1.3 *l*/min.

$$\sigma = \frac{L}{RA} \qquad (4)$$

$$\sigma = \frac{1}{\rho} \qquad (5)$$

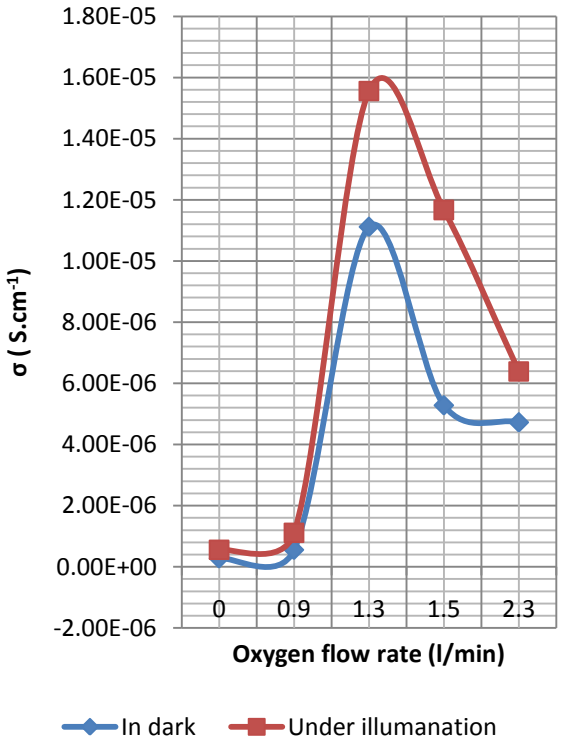

Figure 2: Conductivity vs Oxygen flow rate.

B. *Optical Characterization*

The optical properties such as transmittance and absorbance were also measured. As shown in Figure 3, the absorbance of TiO_2 thin films prepared with oxygen gas flow rate. With an increase of the oxygen gas flow rate, the absorbance of light was reduced. It might be due to the different in thickness of the thin films. The thin films with highest oxygen flow produced the thinnest film with the lowest absorbance, while the lowest oxygen flow produced

the thickest film with the highest absorbance. If the oxygen concentration in the films increases, the coatings become more transparent in the visible region.

The increase of oxygen flow also leads to improved optical absorption, as shown in Figure 3. This trend is likely due to increased light-scattering effects with increasing TiO2 particle size [21].

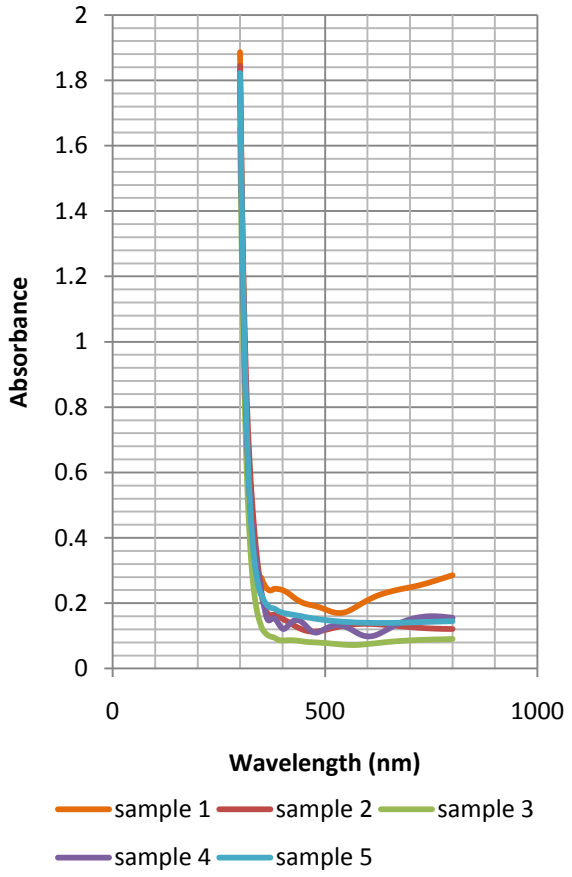

Figure 3: Absorbance vs Wavelength

Figure 4 shows the transmission spectra of TiO_2 thin films in visible region annealed at different oxygen flow rate, which has an obvious influence on the transmission. It is clear from the transmittance curves that with the increase of oxygen flow rate, the optical transmittance gradually increases. With an increase of the oxygen gas flow rate, the transmittance of TiO_2 thin film was improved. The average transmittance in the visible range was above 60%. As can be observed, the optical transparency and the structure of the coatings are both influenced by evolution of the oxygen gas flow rate [22]. Since titanium oxides are optically transparent [23,24], increasing number of oxide bonds leads to increase of the TiO2 film's transmittance.

This is because the transmittance of TiO2 films is related to the absorption of films. And as the absorption increases, the transmittance decreases. One of the main reasons affecting the absorption of the TiO2 films are the substoichiometry of oxidation. The high absorbing suboxide components can be easily formed under low oxygen flow rates, and adequate oxygen can repair oxygen vacancies. The substoichiometry of the TiO2 films induced by insufficient oxygen content is the main cause of transmittance differences. The transmittance of sample 1 that annealed at lowest oxygen flow indicates that the films have more oxygen vacancies.

Surface morphology is another main factor affecting the transmittance of TiO2. The TiO2 films are almost fully oxidized when the oxygen flow is over 2.3 l/min. The higher oxygen flow rates cause the increase in surface roughness of the deposited films, and the transmittance of TiO_2 decreases [25].

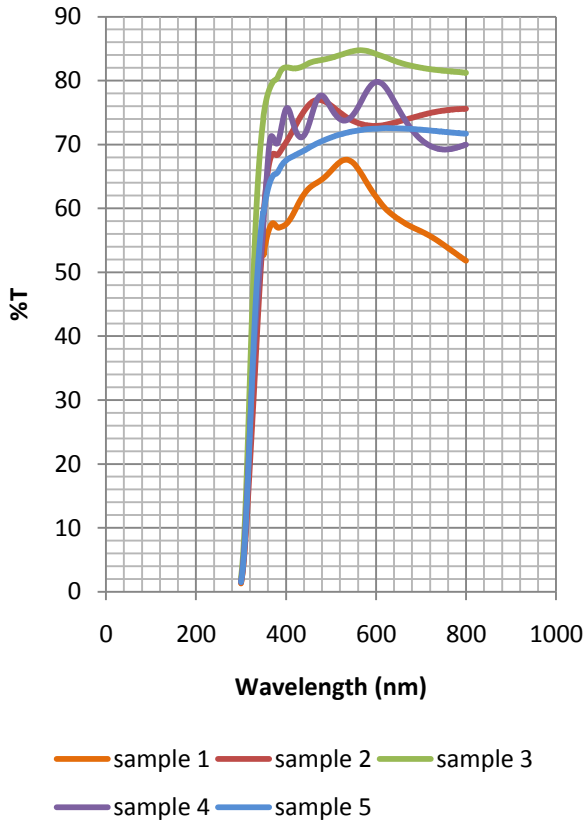

Figure 4: Transmittance vs Wavelength

C. Morphological characterization

Figures 5 show the surface morphology image of TiO2 thin films grown on glass substrates annealed at

different oxygen flow rate. Base on the SEM characterizations, we realize that the TiO_2 thin films become more fragile with the increase of the oxygen flow rate. Another way to explain the low hardness of the TiO2 films is their intrinsic stress. Thus, the intrinsic stress in the films cannot avoid grains boundary sliding or crack propagation during indentation [26].

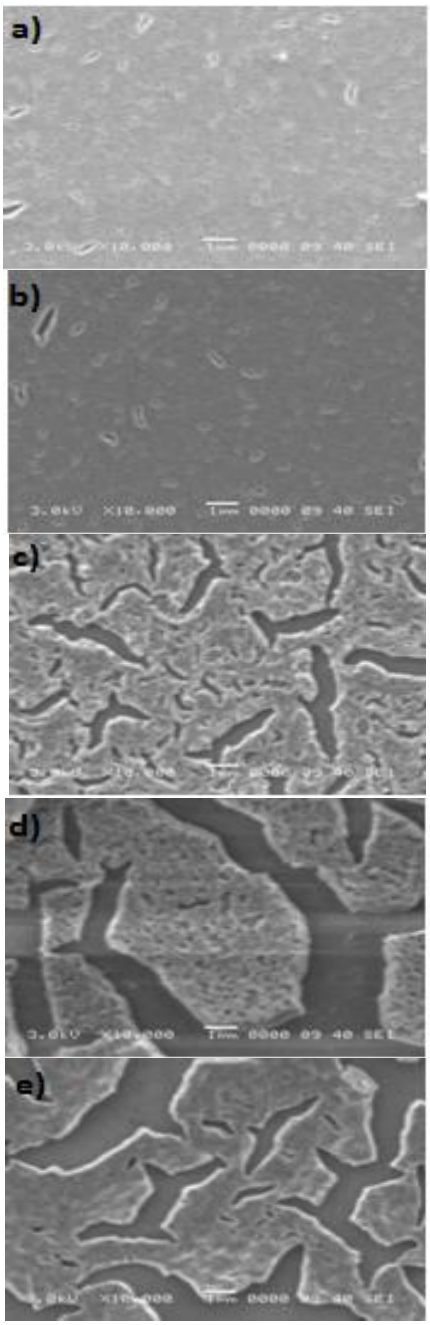

Figure 5 SEM image of TiO2 thin films grown on glass substrates annealed at different oxygen flow rate (a) 0 *l*/*min*, (b) 0.9 *l*/*min*, (c) 1.3 *l*/*min*, (d) 1.5 *l*/*min*, (e) 2.3 *l*/*min*.

IV. CONCLUSIONS

TiO_2 thin films were deposited on glass substrate at oxygen gas flow rate between 0 to 2.3 *l*/min using sol gel method. Sol gel is used because of very economical and simple technique to deposit the TiO2. Base on literature, the preparation procedure of sol gel method may be great influenced the structure of material, especially the different conditions of annealing may cause change in concentration of chemical defects, micropores and grain. Procedure of preparation also may influence the size of grains and micropores. The film thickness can be controlled by the number of coatings. A detailed study of structural, optical and electrical properties of the TiO2 thin films using various experimental tools provided an insight into the effect of oxygen flow rate on the physical properties as well as photoconductivity of the films. The major observations of this study can be summarized as follows. The overall effect of annealing at different oxygen flow rate as well as the resistivity and conductivity in dark and illumination were discovered. The oxygen absorption has a great influence on photoconductivity. As reported in the literature, it found that the transmittance is strongly influenced by film thickness, oxygen flow rate and surface roughness. The thin films become fragile and more transparent with increase of oxygen flow rate.

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