Electrochromic Properties of TiO_2 Thin Films Deposited by Metal Organic Chemical Vapor Deposition and Sol-Gel Techniques

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TiO_2 thin films have been deposited on different substrates by metal organic chemical vapor deposition and sol-gel techniques from the same precursor; titanium tetra isopropoxide. X-ray diffraction studies show that the deposited films by MOCVD are crystalline in the anatase phase, while films deposited by sol-gel technique are amorphous and transform to the crystalline phase due to annealing. UV-Vis-NIR spectrophotometry has been used to characterize the optical properties of the films. Chronoamperometery and cyclic voltammetry have been used to explore the electrochromic behavior of the deposited films. MOCVD films show superior electrochemical properties compared to sol-gel films.

1. Introduction

The pioneering work carried out by Fujishima and Honda [1] has attracted the attention of researchers to the potential applications of TiO_2 for photochemical devices. Afterwards, titanium dioxide has been used in lithium batteries [2], dye sensitized solar cells [3] photocatalysis [4] and electrochromic materials [5]. Titanium dioxide has three famous polymorphs anatase, brookite and rutile. Rutile is considered the thermodynamically stable phase at high temperatures while anatase and brookite are formed at lower temperatures [6]. Phase transformations either by annealing [6, 7], or by increasing the deposition [8.9] temperature results in the formation of rutile and the transformation is irreversible. Anatase and rutile structures can be described as chains of TiO_6 octahedra where each Ti^{4+} ion is surrounded by 6 O^{2-} ions and both of them show a tetragonal structure but the Ti-Ti bond is longer in anatase than that of rutile and the Ti-O bond shows the opposite[6]. The c/a ratio of anatase is larger than that of rutile while the density of rutile is higher than that of anatase. Due to these structural differences, the former offers an opened zigzag structure for Li ions accommodation and movement between the octahedral voids. Therefore, anatase shows a better electrochemical response than rutile [10].

Electrochromism can be defined as the ability of the material to change its color during a redox reaction under the effect of an external electric field [6]. Accordingly some oxides are classified as cathodic electrochromic materials in which the reduction takes places at the cathode likeWO_3 and TiO_2 while others for example IrO_2 and NiO are anodic in which the oxidation takes place at the anode [7]. This phenomenon is the base of smart windows and used in display devices [5].

The experimental techniques used in studying electrochromic materials are similar in some respects since most of them focus in calculating the quantity of inserted charge and elucidating the accompanying optical change [11-17].However, some reports confirmed that potentiostatic process is favorable than galvanostatict [17] due to better current density distribution of the potentiostatic process although in the galvanostatict process the quantity of inserted charge is controllable [12-15].

Titanium dioxide thin films have been deposited by many techniques for example sol-gel [11-15.18], sputtering [19], CVD [4, 7-9, 20-23], and PLD [24]. In this study, comparison between MOCVD and sol-gel technique using the same precursor under potentiostatic polarization has been carried out.

2. Experiment

TiO_2 thin films have been synthesized using a MOCVD (metal-organic chemical vapor deposition) system. It is a hot wall chemical vapor deposition system equipped with a bubbling chamber for liquid precursors. A 5 cm in diameter and 75 cm long horizontal stainless steel tube chamber is used as a reactor. The reactor has a 20 cm uniform central section which is used for depositing the films to avoid any temperature fluctuations effects. Deposition temperature, 450˚C, has been used to deposit the films. The system is pumped down to nearly 3 mTorr base pressure by a mechanical pump to increase the volatility of the liquid precursor and to reduce the contamination from the air. ITO coated glass substrates of sheet resistance ranging from 5 to15 Ω/□ , normal glass substrate, and silicon wafer have been used for deposition.

$Ti[OCH(CH_3)_2]_4$ (titanium tetraisopropoxide, TTIP of purity 97+%, Alfa Asear) has been selected as the precursor for Ti. The liquid TTIP is filled in a Pyrex bubbling flask and 99.999% Ar is used as the carrier gas. The O_2 gas is introduced into the reactor in quantities ranging from 31-33 sccm causing the pressure to be about 12.8 Torr. The precursor flow rate is then fixed by adjusting the Ar flow rate to reach a total pressure of 15 Torr. All samples are prepared under system pressure of 15 Torr and the precursor temperature is kept at about 80°C.

Sol –gel technique has been used to prepare TiO_2 thin films using the same precursor (TTIP). It was mixed with diethanolamine, and ethanol. The solution was stirred for few hours at room temperature. The obtained sol has been spun on ITO substrates. Then the films have been dried. Annealing has been carried out at different temperatures tell 450°C for 2 hours.

Structural characterizations of the TiO_2 thin films have been carried out by X-ray diffraction (XRD). θ-2θ scans are recorded using Cu Kα radiation. Thickness of the film deposited by MOCVD has been studied by scanning electron microscopy (SEM). Optical transmission measurements have been carried out using a UV-Vis-NIR spectrophotometer in the range 300 to 1100 nm.

Electrochemical measurements have been carried out by using an electrochemical cell. In this cell TiO_2/ITO served as the working electrode (WE), an Ag/AgCl as reference electrode and a platinum sheet as the counter electrode (CE). A 1 M $LiClO_4$ in propylene carbonate solution has been used as the electrolyte. Chronoamperometric measurements have been carried out by using a potentiostat, under a constant voltage of -2V for coloring and +2V for bleaching. The coloring time was 2 min. and the bleaching time was 2 min. Cyclic voltammetery is performed between ±1.5V at a sweep rate of 20 mV/sec.

3. Results and discussion

3.1. Structure

X- ray diffraction patterns for TiO_2 thin films deposited by MOCVD and sol-gel techniques are shown in Figs. (1 & 2). In Fig. (1) TiO_2 is deposited on silicon wafer the peak (112), which belongs to the anatase phase, appears at 38.65^{o}. So, the film demonstrates preferred orientation in this direction. However, the main anatase peak, (101), which should appear at 25.3^{o} is not shown. This texturing is expected in MOCVD technique for TiO_2 since, phase transformation from anatase to rutile takes place by increasing the deposition temperature. Such peaks appear at intermediate deposition temperatures [9, 25]. Taylor et al reported such behavior for samples deposited by the same technique using a high vacuum system [9].Also, we reported it by the same technique for samples deposited on soda-lime glass substrate using a rough vacuum system [25]. At low temperatures the main anatase peak (101) appears, and upon increasing the deposition temperature it diminishes and other peaks like (112), and (004) appear [24]. This change in texture has not been detected when monitoring phase transformation due to annealing in sol-gel or CVD samples [6, 7, 27]. It has been attributed to a relationship between surface energy of the formed face (direction or orientation), and the mobility of adsorbed molecules or atoms on the substrate during the MOCVD deposition process [27]. The crystallite size has been calculated for the (112) peak using Sherrer formula (1):

$$D_{(hkl)} = k\lambda / \beta \cos \theta \qquad (1)$$

where k is the shape factor (0.94) [27], λ is the wavelength of X-ray of Cu Kα radiation, β the full width at half maximum (FWHM) of the (hkl) peak and θ is the diffraction angle. The obtained crystallite size was 52 nm. The thickness of this film was found to be 234 nm by using SEM measurements, using the film deposited on normal glass substrate.

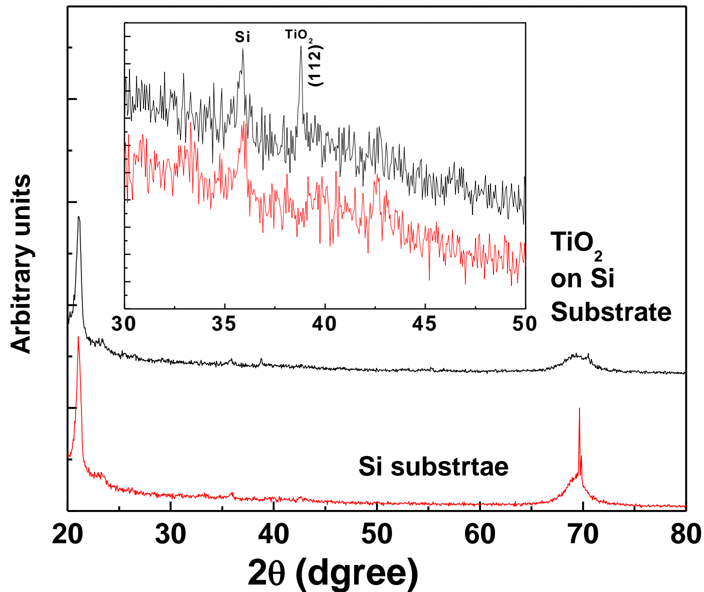

Fig. (1): X-ray diffraction of TiO_2 thin film deposited by MOCVD on Si substrate at 450°C and total pressure of 15 torr in comparison with Si substrate.

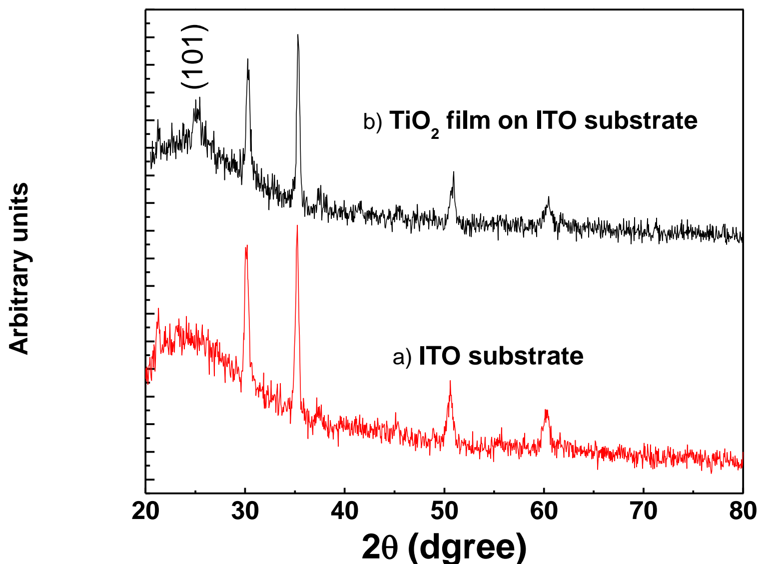

Fig. (2): X-ray diffraction of TiO_2 thin film deposited by sol-gel on ITO substrate and annealed at 450°C for 2 hours in comparison with ITO substrate.

Figure (2) shows the x-ray diffractogram for the film deposited by sol-gel technique and annealed at 450°C for two hours. The main anatase (101) peak appears. Using Eq.1, the crystallite size was found to be 14 nm. Small particle sizes are usually obtained by sol-gel technique [6].

3.2. Optical properties

Transmittance percentage, (%T), versus wavelength spectra for MOCVD film is shown in Fig.(3). At normal incidence the absorption coefficient can be calculated from [19, 28]:

$$\alpha = (1/d) \ln (1/T) \qquad (2)$$

where d is the thickness of the film.
The optical band gap for indirect transition can be calculated from [29]:

$$\sqrt[2]{\alpha h\nu} = (Eg-h\nu) \qquad (3)$$

where **ν** is the frequency of the incident light, h is Planck's constant. Using Eq. 3 the optical energy gap was found to be 3.2 eV, which agrees with the reported value [6, 27]. Fig.(5) shows the transmittance percentage versus wavelength for the sol-gel film. The thickness of the film was calculated using the envelope method, and found to be 196 nm [30]. Using this value and Eq.2 the optical band gap was found to be 3.18 eV.

3.3. Electrochemical measurements

Chronoamperometery for the two films is shown in Fig.(5). It is clear that the area under the curve for the MOCVD film is larger than that of the sol-gel film. This area gives the quantity of the inserted charge using Eq.4:

$$Q = \int I \, dt \qquad (4)$$

where Q is the quantity of inserted charge per unit area (mC/cm^2), I is the current density (mA/cm^2), and t is the coloration time.

The quantity of inserted charge as function of the number of cycles is shown in Fig. (6). It is obvious that the quantity of inserted charge is larger for the MOCVD film. This can be attributed to the thickness and the nature of the film. This conclusion confirms what has been found before for TiO_2 thin films deposited by dip coating [11] and MOCVD using TTIP [27]. The thicknesses of the films are 245 nm, and 230 nm, respectively. For dip coated films at cathodic

potential -3.5 V, Dinh et al [11] found that the quantity of inserted charge after 45 min. of coloration is 56 mC/cm^2 while, for MOCVD under -2V and after the same period of coloration it was 41.3 mC/cm^2. In fact, comparison is not under the exact same conditions but it can be inferred that the MOCVD film shows better results.

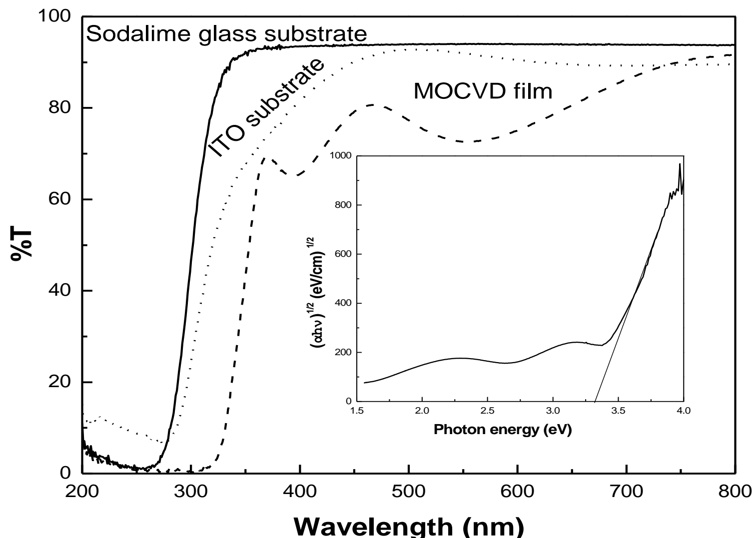

Fig. (3): UV-Vis.-NIR transmittance versus wavelength for normal glass substrate, ITO substrate, and TiO_2 deposited on ITO substrate by MOCVD and the inset shows indirect band gap transition for the deposited film.

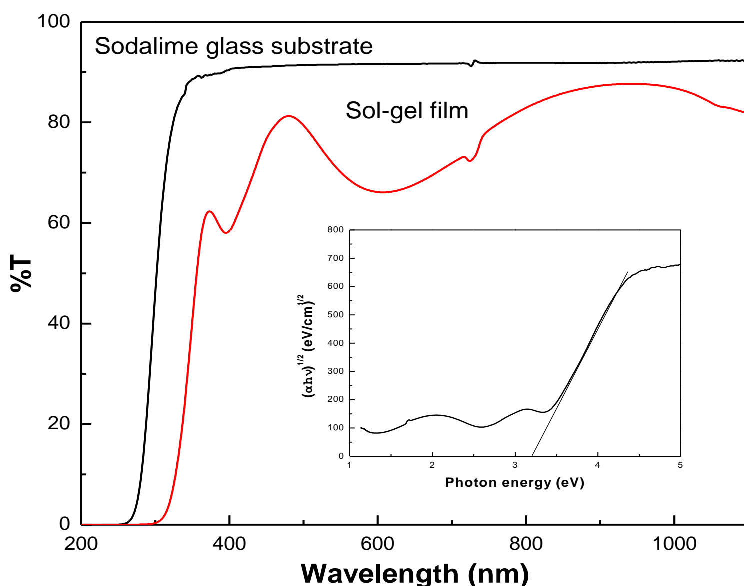

Fig. (4): UV-Vis.-NIR transmittance versus wavelength for normal glass substrate, and TiO_2 deposited on ITO substrate by sol-gel technique and annealed at 450°C and the inset shows indirect band gap transition for the annealed film.

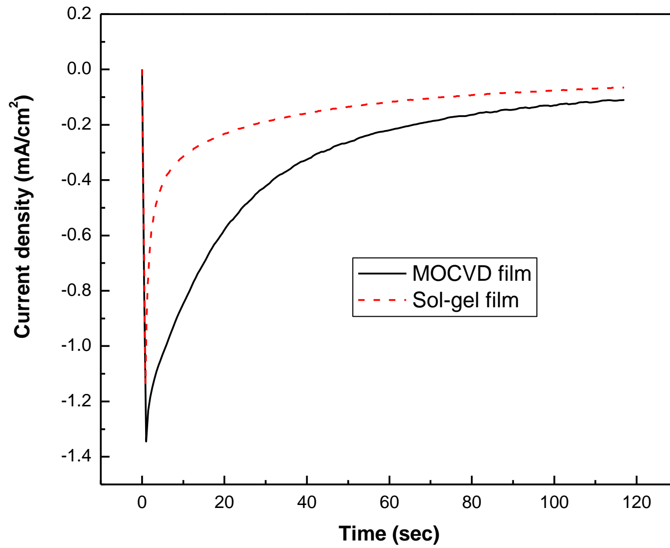

Fig. (5): Current density versus time for films deposited by MOCVD and sol-gel techniques for two minutes.

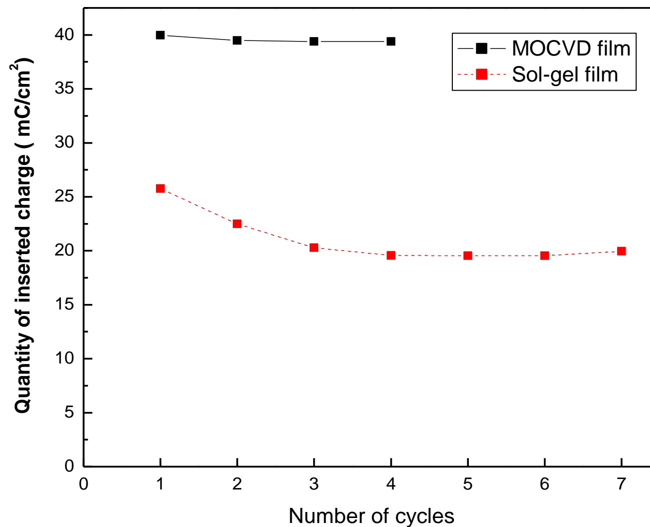

Fig. (6): Quantity of inserted charge versus number of cycles for films deposited by MOCVD and sol-gel techniques.

Cyclic voltammetry has been run for the two films as shown in Fig.(7. 10) cycles has been run. The diffusion coefficient can be calculated from Eq.5. (Randles-Sevčik equation [31]),

$$Ip = (2.69)x10^5(n)^{3/2}CD^{1/2}v^{½} \quad (5)$$

where Ip = peak current density (A/cm^2), n = number of electrons involved in the redox reaction which equals 1 in this case since it compensates the Li ion charge according to Eq. 6, C = concentration of Li^+ in the liquid electrolyte (mol /cm^3)

which has been mentioned earlier as a1 M of $LiClO_4$ in propylene carbonate, v = scan rate (V/s) which has been mentioned in the experimental part as 20 mV /s, and D = diffusion coefficient (cm^2 /s).

$$xLi^{+} + xe^{-} + TiO_2 \leftrightarrow Li_xTiO_2$$
$$\text{transparent} \qquad \text{colored}$$

where x is the mole fraction of Li ions in titanium dioxide.

The diffusion coefficient order of magnitude agrees with that reported in literature [13, 25]. Diffusion coefficient increases with the decrease of particle size for sol-gel electrochromic TiO_2 thin films as reported before by Verma et al [13-15]. Although from XRD measurements the particle size is larger for the MOCVD sample but this is not the controlling parameter here. The nature of the deposited film is the effective parameter in this study. Usually the diffusion coefficient and the cycle area decrease with the number of cycles tell obtaining equilibrium. But the opposite is shown for the sol-gel sample. Verma et al [13] run about 1100 cycles for samples deposited by the same technique and precursor but they did not discuss the behavior of the diffusion peak current with the number of cycles, which suggests further studies in the future.

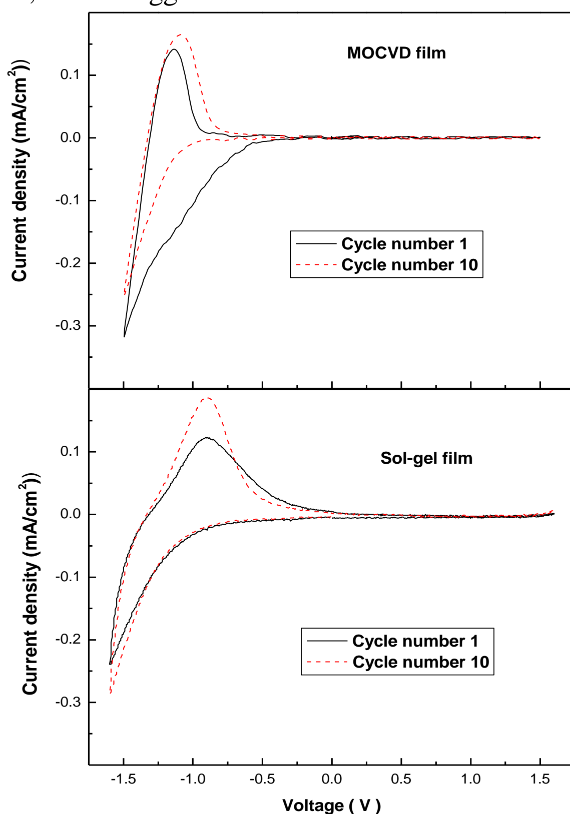

Fig.(7): Cyclic voltammetry curves of samples deposited by MOCVD and sol-gel techniques.

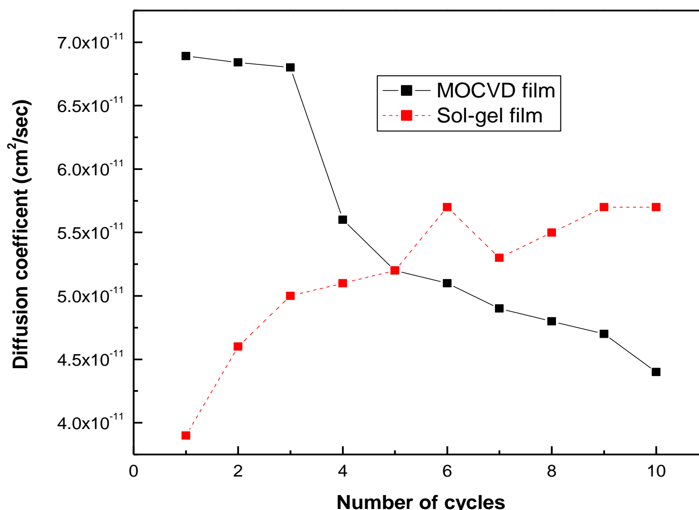

Fig.(8): diffusion coefficient as a function of number of cycles for samples deposited by MOCVD and sol-gel techniques.

4. Conclusion

Nano-crystalline titanium dioxide thin films have been prepared by MOCVD, and sol-gel techniques. Characterization by XRD reveals that the obtained phase is pure anatase. Indirect band gap transition has been found to fit well the spectrophotometric data. Electrochromic and electrochemical performance have been tested by a potentiostat in an electrochemical cell. The MOCVD film shows a larger quantity of inserted charge compared to the sol-gel film. Cyclic voltammetry ranges in the same order of magnitude for the two films.

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