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Effect of calcination and pH value on the structural and optical properties of titanium oxide thin films

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Titanium oxide thin films on glass and silicon wafer substrates were prepared by the sol-gel process. The pH variation and the calcination effect on the optical and structural properties of the films were systematically examined. The coated films were characterized by atomic-force microscopy (AFM), NKD analyzer, X-ray diffraction (XRD) and cyclic voltammograms (CV). The influence of calcination and pH value on the spectra of transmittance, reflectance, and refractive indices and on the surface structure has been investigated. From X-ray diffractometric measurements (XRD), it has been confirmed that the films are an anatase form. The effects of pH and surface modification of titanium oxide were studied with AFM images. These showed that the surface texture was changed dramatically according to calcinations and pH variation. Spectral dependencies of refractive indices (*n*) were determined for all films. Band-gap energy (E_g) was also estimated for these films.

1. Introduction

Titanium oxide film has been extensively investigated with regard to its remarkable optical, electronic, and chemical properties. Titanium oxide films have been shown to possess electrochromic property. Electrochromic materials change their optical properties in response to an electric field and can be returned to their original state by a field reversal. The recent interest in films with an anatase crystalline phase has led to applications in environmental cleaning, such as a photocatalytic purifier [1–3], and in solar energy converters, such as a photochemical solar cell [4]. Other applications include humidity and gas sensors, and gate electrodes in semiconductors [5]. TiO_2 films have been prepared on different kinds of substrate by many researchers [6–11]. One of the TiO_2 films grown on glass has many commercial applications such as self-cleaning, anti-bacterial and waste water purification containment [12–15]. The preparation of TiO_2 film on glass has been conducted by using different techniques such as pulsed-laser deposition [16], sputtering [17] and sol-gel [18]. Sol-gel technique has attractive characteristics for the preparation of high quality thin film because of its ability to control deposition parameters. This method produces samples with good homogeneity and reproducibility, enabling us to coat substrates of any size. It is expected that TiO_2 on high quality film can be prepared by controlling deposition parameters such as pH value, viscosity, substrate temperature and thickness. The preparation of TiO_2 film on glass using several deposition techniques had been studied [19]. It is well known that the structural, optical and electrochemical properties of transition metal oxide films, namely the morphology, directly depend on the deposition routine [20, 21]. Although there are a number of studies which examine the effect of deposition parameters on the microstructures of titanium oxide films [19], the morphology and the optical and electrochemical properties of TiO_2 films have not been elucidated in relation to the deposition parameters pH values and calcination temperatures.

The aim of the present work is to show the effect of the preparation conditions such as calcination and pH values on the structural, optical and electrochemical properties of the films. For this purpose titanium oxide thin films were prepared under different conditions on silicon wafer and ITO coated glass and glass substrates. The effect of the preparation conditions on film morphology, optical and electrochemical properties were characterised using dynamic AFM mode, XRD, NKD analyzer and CV respectively. In order to examine the effects of preparation conditions on the structural, optical and electrochromic properties, a detailed systematic study of titanium oxide thin films has been carried out using TiO_2 sols having different pH values coated on different substrates. These were annealed at progressively increasing temperatures ranging from 100 to 920°C in oxygen environments.

2. Experiment

Titanium oxide films were deposited by a spin-coating procedure. The TiO_2 films were prepared on ITO

TABLE I The pH values of sols used in this study as a function of the amount of acetic acid

Amount of acetic acid (ml)	pH value
100	5.67
150	5.30
200	4.99
250	4.26
300	4.20
350	4.02

(Indium Tin Oxide) conductive transparent glass, Corning glass (2947) and silicon-wafer substrates. The substrates were cleaned with detergent and flushed with copious amounts of de-ionized water. Finally the substrates were sequentially rinsed with acetone, methanol and isopropyl alcohol and dried in air. The coating solutions were prepared by dissolving 1.2 ml titanium (IV) butoxide in 15 ml ethanol solution with stirring for 1 h. Initially 50 ml acetic acid was added to the solution as a catalyst. After preparing the titanium oxide solution as described above, the solution was separated equally into seven beakers of approximately the same volume. Various amount of acetic acid were added to the beakers such as 100, 150, 200, 250, 300 and 350 ml in order to obtain sols with different pH values. 10 ml ethanol was added to the solutions after 1 h and stirred for 2 h. The obtained sol was initially transparent. Thus seven different pH value sols were obtained by adding different amounts of acetic acid: 50, 100, 150, 200, 250, 300 and 350 ml. The pH values of sols used in this study were given in Table I as a function of the amount of acetic acid. Several hours later, the sol with 50 ml acetic acid lost the transparency and became gel. The transparent sols were applied to the substrates using a spinner. The samples were prepared by spin coating at 2000 rpm spin speed. Multiple depositions of up to five layers were carried out to increase the thickness. The intermediate annealing step in air was necessary to prepare crack-free thick films. Each layer was fired for about 30 min at 100°C before a subsequent coating. The thickness of the as-deposited samples was approximately 100 nm. Some of the as-deposited TiO_2 films were subsequently subjected to heat treatment at different temperatures (100, 200, 300, 500, 760, and 920°C) for 2 h in air.

The crystal structure of the films was analyzed by a Philips PW3710 X-ray diffractometer with the Cu K_α radiation from 10 to 60° in steps of 0.02°. The surface morphology of the films was examined using an atomic force microscope (AFM), SPM-9500 Series Shimadzu in the dynamic mode. The transmittance and reflectance of the films was measured using an NKD Aquila Instrument. The spectral range from 300 to 1000 nm at a 30° angle was used for measuring the optical transmittance and reflectance values of the films. Electrochemical experiments were conducted with an EG&G Princeton Applied Research Potentiostat Model 273. 1 M $LiClO_4$/PC, a SCE, a platinum wire and ITO coated glass were used as the electrolyte, as the reference electrode, as the counter electrode and as the working electrode respectively. Viscosity of the sol was measured using a Brookfield DVIII + type low-shear viscometer.

3. Result and discussion

The crystal structure of the films coated on silicon wafer and glass substrates was examined using an XRD, as shown in Figs. 1 and 2 respectively. All samples coated on silicon wafer substrates were in the anatase phase, except the amorphous one which was heat treated at 300°C (Fig. 1). The XRD data shown in Figs. 1 and 2 indicate that the samples prepared on silicon wafer substrates heat treated at 500, 760 and 920°C have anatase structure, those prepared on glass substrates heat treated up to 500°C have very weak peaks which indicate that the films have very small crystallite size. On glass substrates, the crystal structure is difficult to recognize from the diffraction patterns due

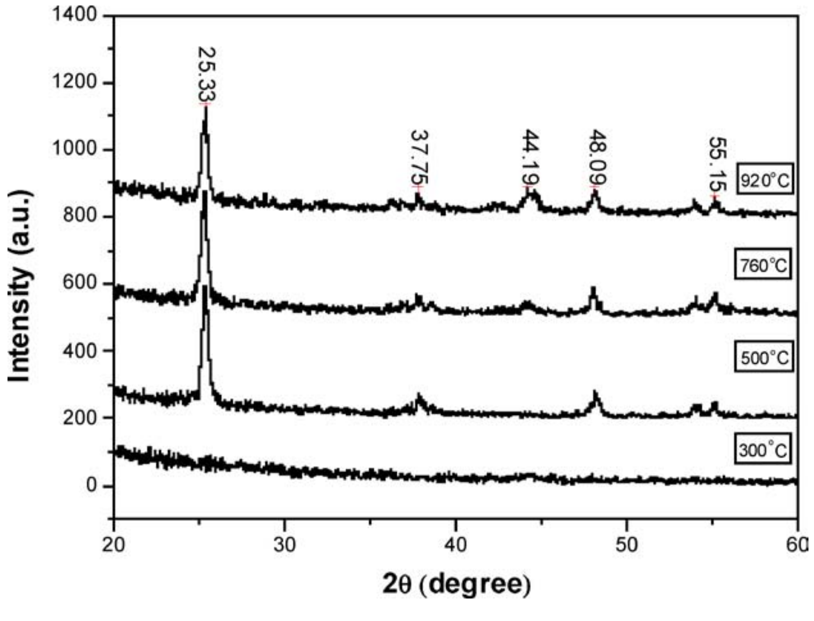


Figure 1 XRD patterns of titanium oxide thin films on silicon-wafer substrates annealed at different calcination temperatures (300, 500, 760 and 920°C).

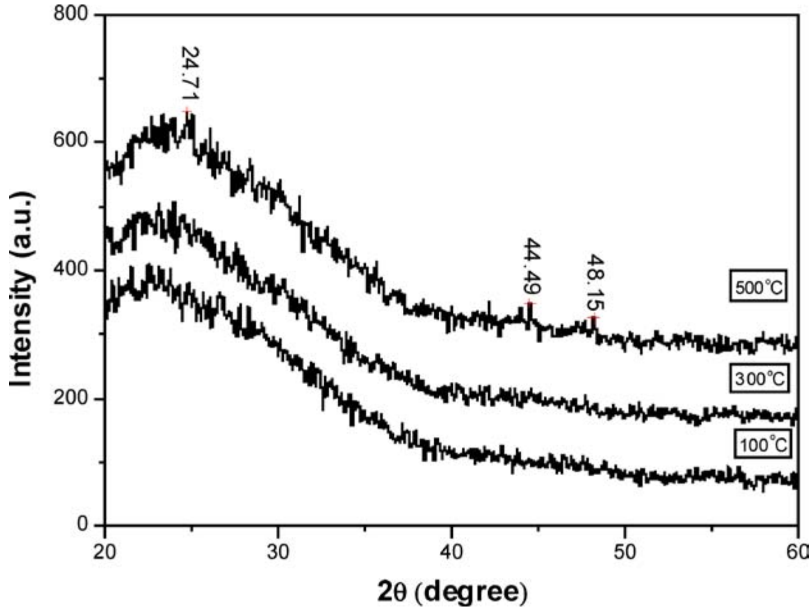


Figure 2 XRD patterns of titanium oxide thin films on glass substrates annealed at different calcination temperatures (100, 300 and 500°C).

to low X-ray intensities. This amorphous structure could be a result of the migration of Na^+ ions from the glass substrate. The layer might behaved as barrier layer and Na^+ ions were confined into this layer. So the crystal formation is influenced by the type of substrates. On the other hand the anatase form is stabilized after calcinations up to 920°C for the samples prepared on silicon wafer substrates. It is well know that the anatase–rutile transformation depends on impurities, grain size, reaction atmosphere, and synthesis conditions [22–25]. Yang *et al.* [23] showed that synthesis conditions affect the crystallinity and anatase–rutile phase transition temperature. Zaban *et al.* [24] noted that the surface structure of TiO_2 is affected by the preparation conditions. Ahonen *et al.* [25] observed that anatase synthesized in air transformed to rutile at 973 K. The anatase form is observed up to 920°C for all samples coated on silicon wafer substrates. This is due to the preparation route and retards the anatase to rutile transformation for the samples coated on silicon wafer substrates.

Figs. 3–5 are the AFM images of TiO_2 thin films grown on silicon wafer and glass substrates at different calcination temperatures and pH values. AFM images of TiO_2 thin films grown on silicon wafer and glass substrates at different calcination temperature with the same pH value (4.26) are provided in Figs. 3 and 4 respectively. AFM images of TiO_2 thin films grown on glass substrates at different pH values with the same calcination temperature (100°C) are shown in Fig. 5. The surface morphology of TiO_2 films coated on the glass substrates is smooth with a roughness of 0.198-0.497 nm. As the pH value of the sol decreases, the surface roughness increases (Table II). At high calcination temperature, the surface morphology of the film roughens on glass substrates as shown in Table III. Silicon wafer substrates were used for higher calcination temperatures. AFM images show that films coated on silicon wafer substrates have a granular structure different from those on glass.

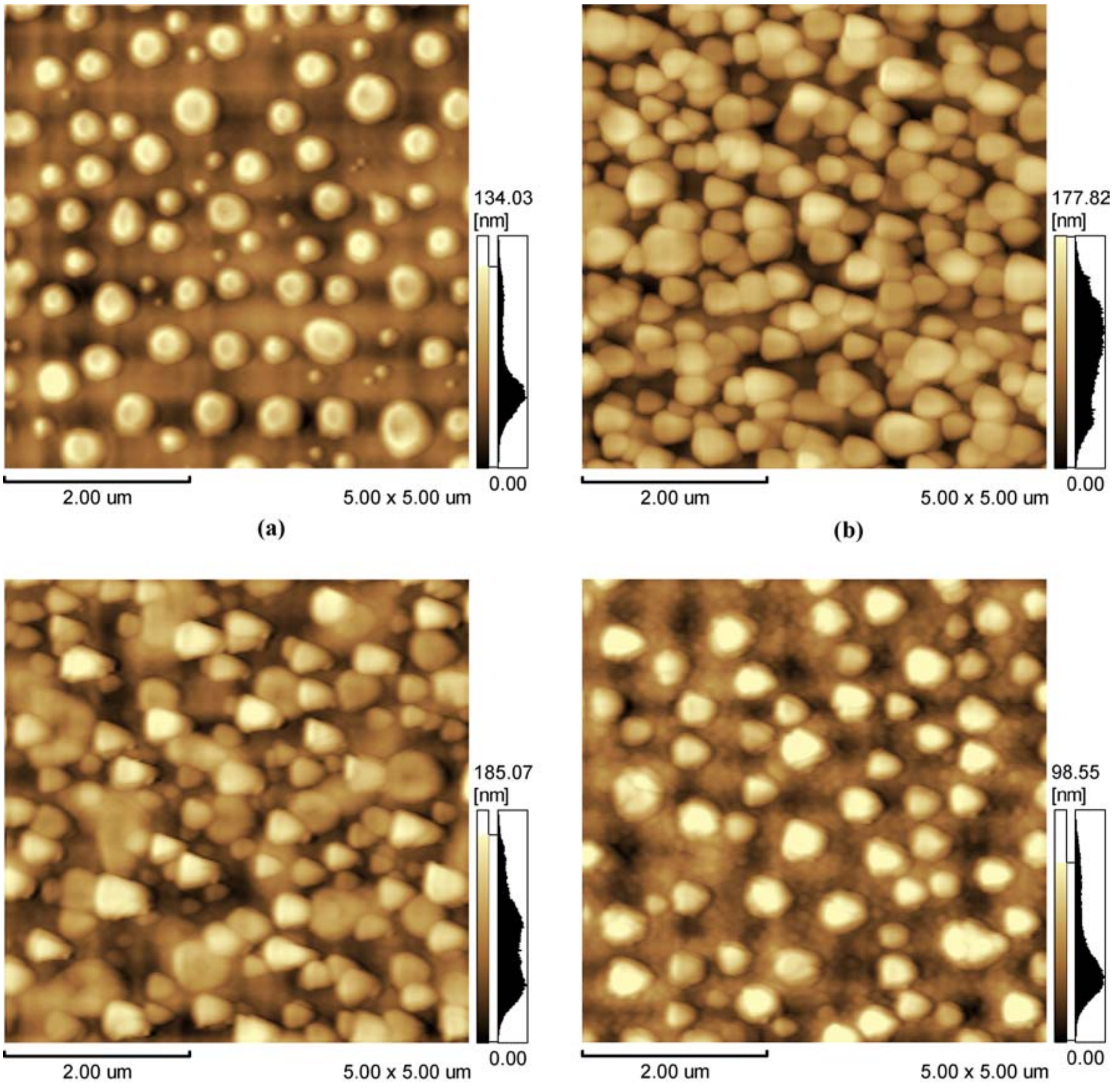
TABLE II The average surface roughness (R_a) of the TiO_2 films as a function of the pH value of the sol

pH values	R_a (nm)
5.67	0.223
5.30	0.260
4.02	0.375

TABLE III The average surface roughness (R_a) of the TiO_2 films as a function of the calcination temperatures

Heat treatment temperature (°C)	R_a (nm)
500	0.497
300	0.456
200	0.211
100	0.198

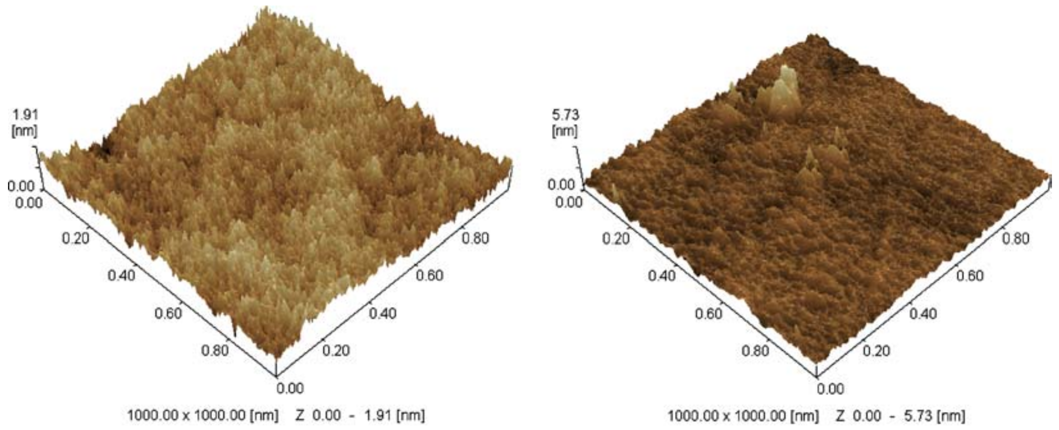
An NKD (refractive index, extinction coefficient and thickness) analyzer was used to evaluate transmission and reflection intensity of the prepared films between 300 and 1000 nm. Package software in the NKD system was used to extract the optical constants of these films. Fig. 6a reveals the transmittance and reflectance of TiO_2 film heat treated at 100, 300 and 500°C, where Fig. 6b compares the transmittance and reflectance of TiO_2 films at 5.67–4.02 pH values. The transmittance of TiO_2 film on glass substrates decreases with increasing calcination temperature (Fig. 6a). This fact was supported by AFM images (Fig. 5) of films prepared at lower calcination temperature (100°C) which result in smooth surfaces, while those films prepared at higher calcination temperature have rough surfaces. The thickness of the TiO_2 films decreases linearly from 100 nm to 55 nm with an increase in heat treatment temperature from 100 to 500°C. The average transmittance of the films is less than 90% for the films heat treated at 100°C. All films prepared at 100°C with different pH values are highly transparent, as shown in Fig. 6b. The structural defects such as pores and grain



(a) (b)

(c) (d)

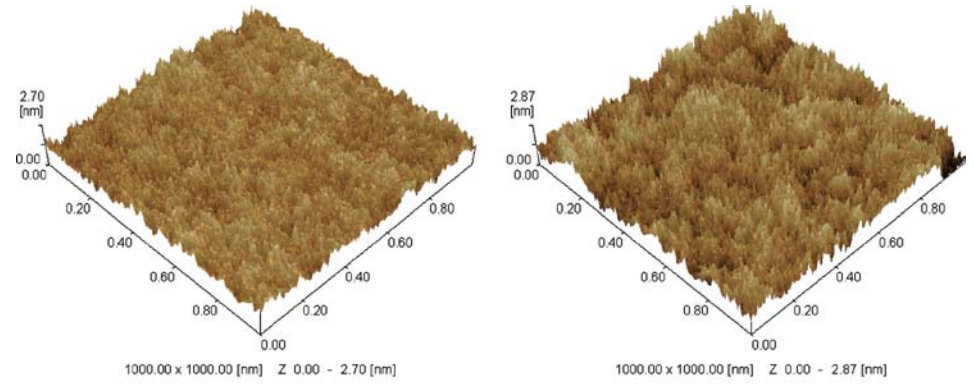
Figure 3 AFM images of TiO_2 films prepared on silicon wafer substrates at (a) 100°C, (b) 500°C, (c) 760°C, and (d) 920°C for 2 h with the same pH value (4.26).



(a) (b)

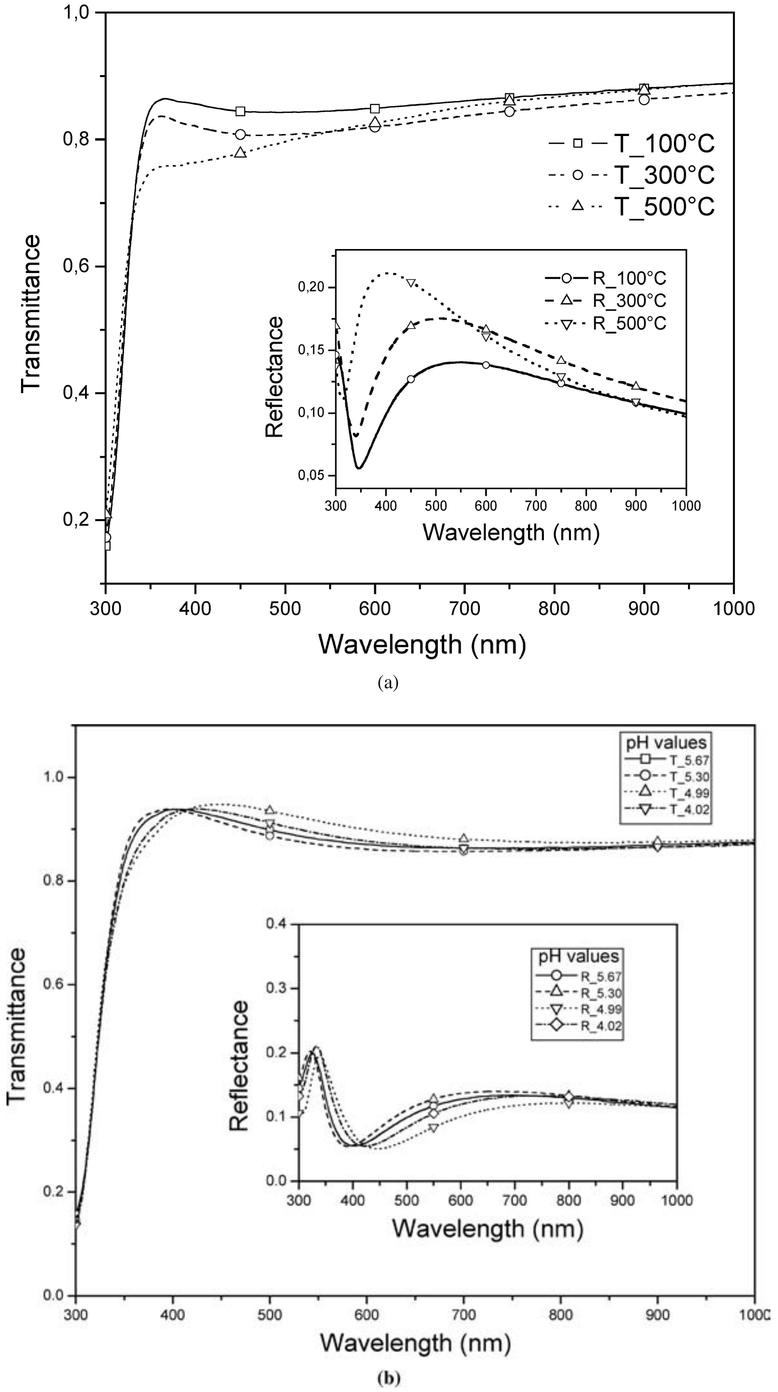
Figure 4 Three-dimensional AFM images of TiO_2 films prepared on glass substrates at (a) 100°C and (b) 500°C for 2 h with the same pH value (4.26).

boundaries play a role as light scattering center. Such high transmittance is may be due to the surface roughness and density of the film. The thickness of the films prepared with various pH values sol at 100°C is almost same as 100 nm. Refractive indices versus wavelength graph of the films are given in the Fig. 7a and b. From Fig. 7a for the films heat treated at 100, 300 and 500°C (pH: 4.26), it is found that the refractive



(a) (b)

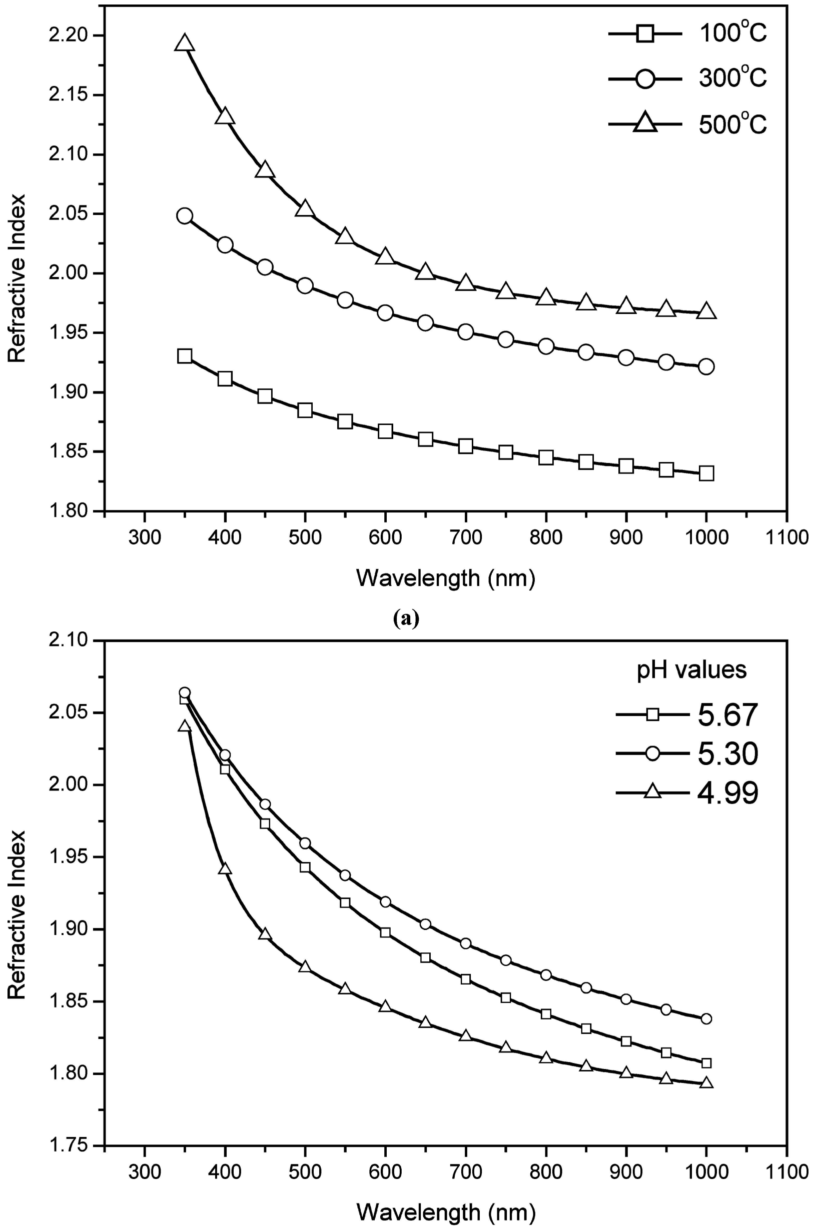
Figure 5 Three-dimensional AFM images of TiO_2 films prepared on glass substrates at 100°C with different pH values (a) 5.67 and (b) 4.02.



(a)

(b)

Figure 6 Transmittance and Reflectance Spectra of TiO_2 films at (a) 100°C, 300°C, 500°C with the same pH value (4.26) and (b) various pH values 5.67–4.02 (100°C)



(a)

(b)

Figure 7 Refractive index of TiO_2 films at (a) 100°C, 300°C, 500°C with the same pH value (4.26) (b) various pH values 5.67–4.02 (100°C).

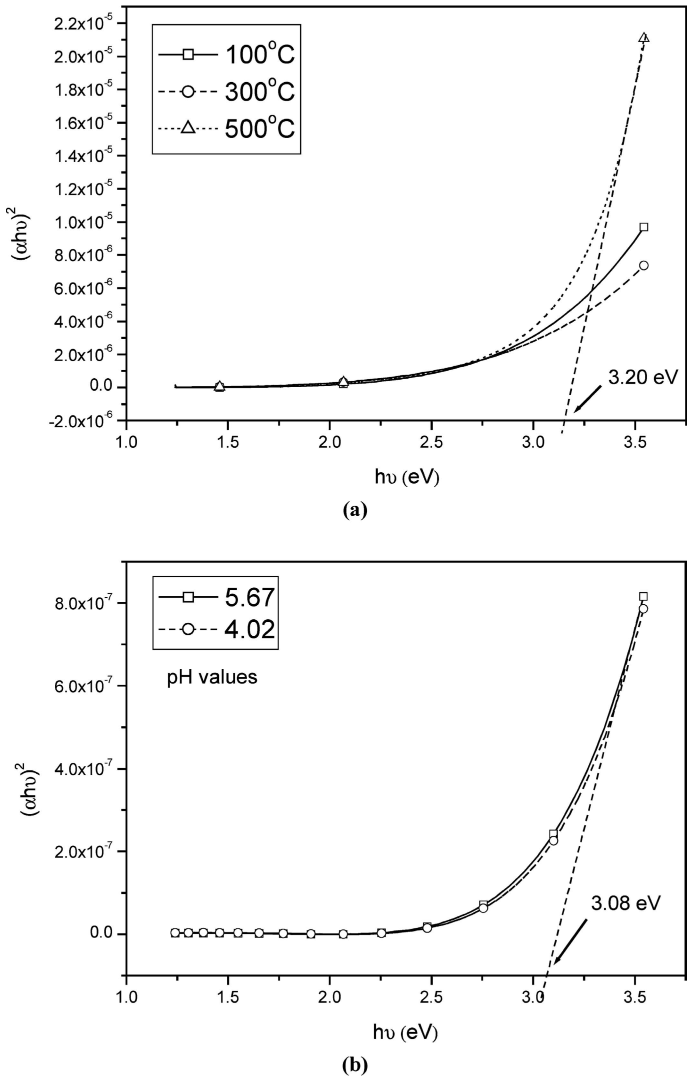
index increased with increasing calcination temperature. Refractive indices values of spin coated films were found 1.87, 1.97 and 2.02 for 100, 300 and 500°C at 550 nm respectively. There was no remarkable correlation between the refractive indices of the films and pH values.

In order to understand how the band gap is affected by the change of pH values and then calcination temperature, the band gap of the films was calculated using Equation 1 [26] as follows.

$$\alpha = (h\upsilon - E_g)^m \tag{1}$$

where α, E_g and m ($= 2$) are the absorption coefficient, the optical band gap and a constant, respectively. The calculated band gaps are plotted in Fig. 8a and b. The films have band gap energy of 3.08 eV for different pH values films heat treated at 100°C. There is no change of band gap with various pH values. The film coated on glass substrates heat treated at 500°C has band gap energy of 3.20 eV. This value is comparable to the band gap of anatase. This result is in good agreement with the XRD data which shows that the film heat treated at 500°C has an anatase structure as shown in Fig. 1a. It is clear that the band gap of TiO_2 film heat treated at different temperature shifts to higher energy and those prepared at different pH values has the same band gap energy.

More acetic acid addition stabilized the solution and greatly facilitated the synthesis of the precursor solution. The sols which were prepared with more acetic acid, both 300 and 350 ml, are stable for more than three months. The sols prepared with less acid gelled by reaction with moisture in air. The viscosity of the most stabilized solution (pH value: 4.02) was also calculated as 2.25 mPa s.



(a)

(b)

Figure 8 The band gaps of TiO_2 films at **(a)** 100°C, 300°C, 500°C with the same pH value (4.26) and (b) various pH values 5.67 and 4.02 (100°C).

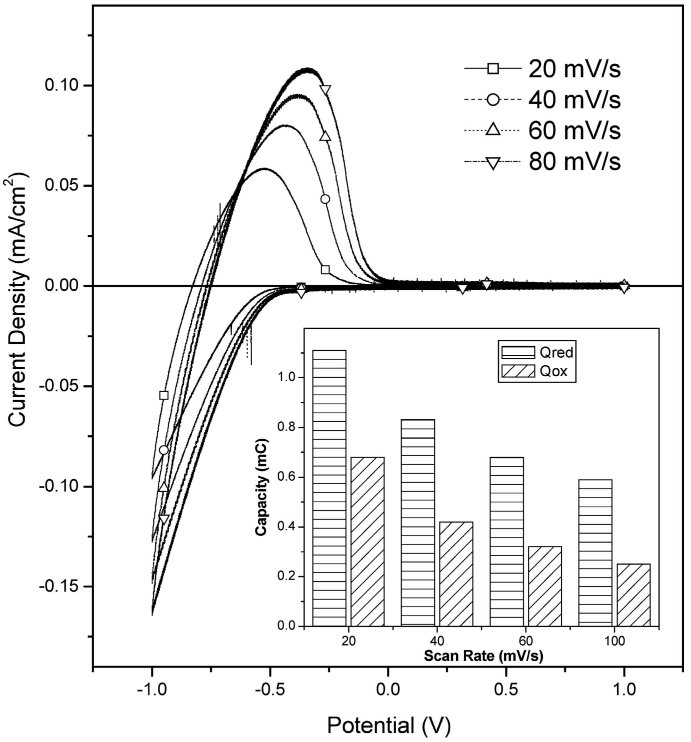


Figure 9 Cyclic Voltammetry for TiO_2 films heat treated at 100°C (pH value: 4.02) with respect to various scan rates. As an inset is reported the determination of the capacities $Q_{ox.}$ and $Q_{red.}$ from a CV of TiO_2 thin films.

We subsequently employed the potentiostatic method to study the electrochemical kinetics of the titanium oxide films. Typical cyclic voltammetry results for TiO_2 films which were prepared with most stable sol are given in Fig. 9. The cyclic voltammograms of the TiO_2 coated on ITO substrates demonstrate good electrochromic properties. The titanium oxide film capacities $Q_{\text{red.}}$ (reduction) and $Q_{\text{ox.}}$ (oxidation) deduced from the CVs (inset of Fig. 9) are shown in Fig. 9. The capacity Q_{red} and Q_{ox}. corresponds to the reduction and oxidation process respectively. The charge capacity of TiO_2 was obtained as 1.11 mC at the scanning rate of 20 mVs^{-1}. While no cathodic peaks are observed, there is a well-defined anodic peak for the sample, indicating the lithium insertion-removal process is highly reversible. In addition, the anodic peak does not shift to higher potentials. This exhibits the apparent improvement in kinetics.

4. Conclusion

The effect of calcination and pH values on the structural, optical and electrochemical properties of TiO_2 films was systematically examined. Increasing amount of acetic acid stabilized the sols. The stability of sol was more than 6 months, which makes them useful and suitable for industrial applications. XRD pattern of the TiO_2 thin films shows that the as-deposited films at low deposition temperature (up to 300°C) are amorphous. Samples prepared on silicon wafer substrates have anatase structure and those prepared on glass substrates heat treated up to 500°C have very weak peaks which indicate that the films have very small crystallite size. The surface morphology and crystal structure of TiO_2 films was influenced by calcination temperature and pH value during fabrication. The refractive indices of TiO_2 increase with increasing calcination temperature as a result of less grainy compact structure on glass substrates. At all pH values, the films have band gap 3.08 eV. Changing heat treatment temperatures, lead to change in the energy band gap. The CV of the TiO_2 films demonstrates good electrochromic properties.

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