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Effects of Annealing Temperature on Anatase-Rutile TiO_2 Multilayer Thin Films prepared by Sol-Gel Spin Coating Method

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Abstract

Titanium dioxide (TiO_2) multilayer(ML) thin films (2-layers) have been deposited on glass substrate by using Sol-Gel Spin Coating technique. The influence of annealing temperature on the structure, surface morphology, optical and electrical properties of these films are characterized by Raman, XRD, FT/IR, UV-vis and four-point-probes measurements. XRD results indicate that ML TiO_2 thin films has formed anatase crystal structure at (101) plane and the (101) grain size is increased when the annealing temperature have been increased. The electrical properties by four point probe measurements showed that resistivity decreased with an increase in the annealing temperature. The SEM result indicated that the lattice matching between TiO_2 and substrate is important to produce good quality ML TiO_2 thin film after annealing process. Optical properties of the films were measured by UV–Vis spectroscopy which showed the high transmittance in the visible region. The optical band gap energies decreased with increasing annealing temperature. It is suggested that the surface porosity, electrical properties and surface morphology of ML TiO_2 thin films could be affected by changing the annealing temperatures for electroluminescence device application. Moreover, the multilayer films of TiO_2 can enhance the properties of optoelectronic devices.

Key Words: **Sol-gel; Multilayer TitaniumOxide (MLTiO$_2$) and Electrical properties**

I. INTRODUCTION

Titanium dioxide (TiO_2)is the most attracted materials innano-technology because of having a lot of interesting properties [1]. TiO_2 thin films have received much interest for the applications such as optical devices, sensors,refractory, wear and corrosion-resistant coating and solar cell. Titanium dioxide is also a promising oxide material with useful electrical and optical

properties and also excellent transmittance of visible light[2-4].There are numerouscauses in determining important properties in the performance of TiO_2 for above applications such as particle size, crystallinity, electrical, optical and the morphology[5-7].Forthe creation of TiO_2 thin films, there are numerous methods established such as sol-gel technique [8], hydrothermal method [9], chemical vapor deposition [10-11]direct oxidation method and others[12-13]. Sol-gel Spin coating technique is one of the most versatile methods due to its possibility of growing unique metastable structure at low reaction temperatures and excellent chemical homogeneity [14]. The crystallization and oxide film development effected by the thermal treatment of the adjusted sol-gel. Titanium tetraisopropoxide produced high hydrolysis and polycondensation rates and precipitated into condensed particle when combined with water. Chemical modification of alkoxides with different agents is very important in sol-gel method. It can change the formation of new molecular precursors that can produce a wide range of new properties. The sol–gel technique has emerged as a new and promising processing route for nano-sized TiO_2 thin films production because of its simplicity. For many technological applications, low processing temperature is highly desirable because it enables the use of certain substrate materials and/or prevents harmful film–substrate interaction. In other hand, the sol–gel processing starting from metal alkoxide or some other metal–organic precursors still requires processing temperatures in excess of 400ºC for the crystallization and removal of organics. The strong reactivity of the alkoxide towards H_2O often results in an uncontrolled precipitation and limiting the use of the sol–gel technology. These problems have been overcome with the aid of chelating agents, such as acetic acid[15]. Amorphous and polycrystalline forms of TiO_2 can be readily prepared using the sol-gel technique[16] which offers the possibility of relatively low cost, large-scale production of thin films. Many researchers have identified significant interactions between process parameters such as withdrawal rate, sol-concentration and the number of coating layers and their effects on structural, optical and electrical properties of sol-gel derived TiO_2 thin films[17]. To optimize the properties of TiO_2 films, the films must be prepared to enhance crystallinity. However, the as-deposited TiO_2 films are often mainly amorphous when the substrates are not heated during spin coating process, and this is the manner adopted industrially. So it is necessary in the preparation of TiO_2 films to anneal them after spinning to improve their crystallinity, thus achieving TiO_2 films optimum for applications in photo-catalysis, dye-sensitized solar cells, and photo-induced hydrophilicity[18-21]. On the other hand, the heat treatment can produce other effects on film structure, resulting in changes in some properties and chemical composition. Many annealing parameters, such as the atmosphere annealing time and temperature schedule, can affect the film structure. The coatings of thin films are used to enhance the energy efficiency and color of glass and as reflecting mirror coatings of glass [22-24]. Since the use of single layer thin films in various devices have increased. There are a lot of applications that require the multilayer films which combine different properties of various materials because of its excellent optical, electrical properties such as dielectric constant, high refractive index, large band gap and high transmittance in the visible region spectrum [25-27]. These properties make it suitable for multilayer thin films [28]. Multilayer thin films have potential applications in different devices, some of which are in the design of computer disks, optical filters and solar cells [22- 23].

In this work, multilayers (2-layer) TiO_2 thin films were prepared on glass substrates using sol-gel spin coating method. After that, the films were annealed at 50°C, 75°C, 104°C, 136°C, 176°C and 200°C for 1 hour.

The structural, optical, morphological and electrical properties were investigated by XRD, Raman, FT/IR, SEM and AFM.

II. EXPERIMENTAL

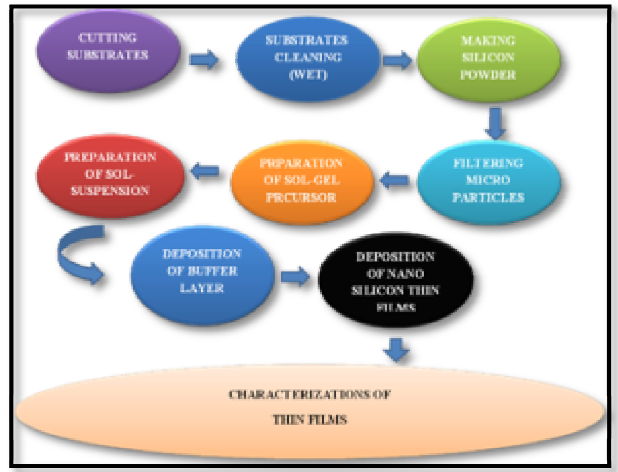
A. Substrates preparation

TiO_2 thin films were prepared by the sol–gel spin coating technique. Fig. 1a shows the block diagrams of step by step experimental procedure at a glance. Fig. 1b shows the spin-coater set up used in this experiment. Nitrogen (N_2) gas cylinder as a back pressure is connected to the liquid dispenser. Sol-gel liquid holder is also connected to the liquid dispenser with a stand just above the spin coater stage as shown in Fig 1b. Adjusting the back pressure, the amount of precursor liquid (0.2 ml) can be disseminated on the mounted substrate in the spin coater. In these work, Corning 7059 glass substrates were used for different measurements. The sample preparation processes can be divided into two steps: (1) The substrates were cleaned for 15 min using acetone, 15 min using ethanol and 15 min using DI water in an ultrasonic cleaner,

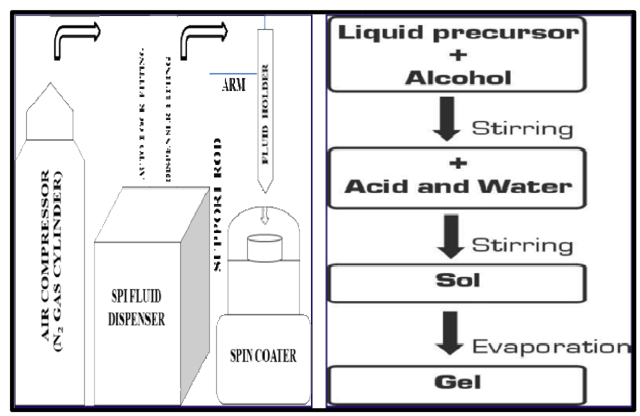
B. Sol-gel preparation process

Step 1(**Acid-water**):
1 ml of Hydrochloric Acid (Hcl) mix with DI (deionized) water) with 1:1 ratio (e.g.Hcl : DI = 0.5 ml:0.5 ml) was prepared

Step 2 (**Solvent-Solution**):
Titanium Isopropoxide(TIP) mix with Absolute Ethyl Alcohol (AEA) having the ratio of (TIP:AEA) 1:8was prepared and stirring. Few min later, adding the pre-prepared acid waterwith the solvent-solution and the mixture is vigorously stirred using a magnetic stirrer for 2 hrs (GEL) at room temperature to get homogeneous solution of TiO_2. Then the TiO_2 sol-gel is ready for thin film deposition.



(a)

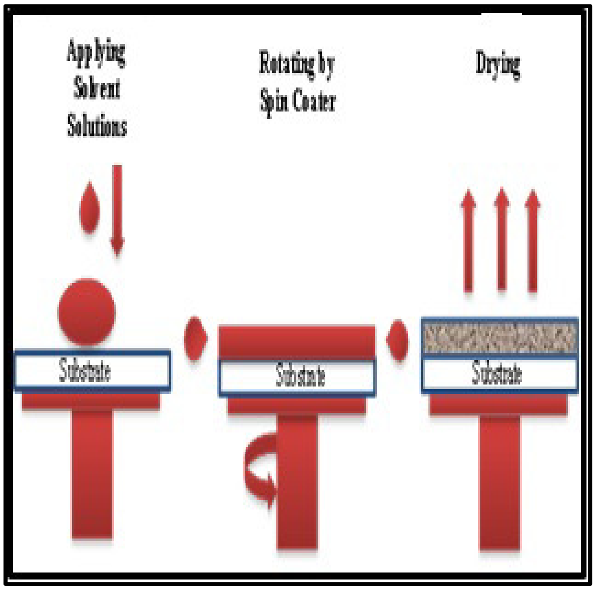


(b)

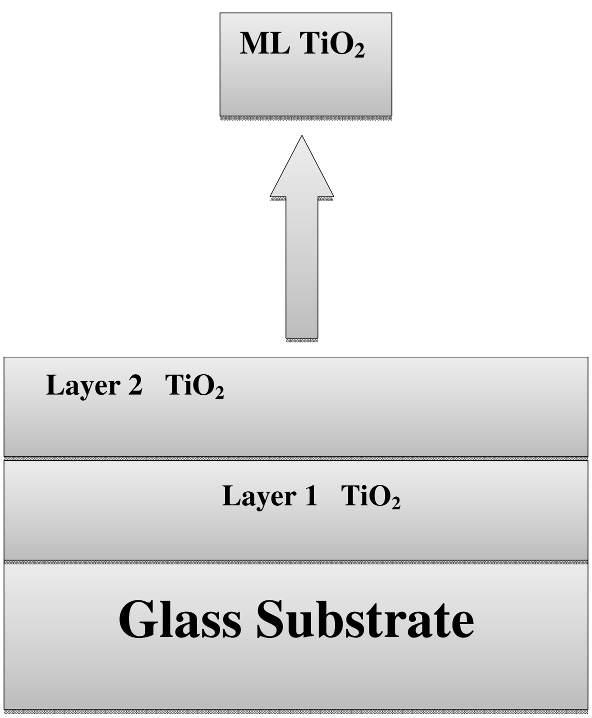
Fig.1 (a) Overall steps and (b) Schematic diagram of the Spin coater set up used in this experiment

C) Synthesis of Thin films

To make multilayer thin films with this prepared homogeneous TiO_2 solution, spin coating device was used. The glass substrate was fixed on spin coating disc and its speed was adjusted at 18,00 rpm.0.2ml of TiO_2 solvent-solution was released from the sol-gel holder located just above the spin coater on the glass substrate and TiO_2 thin film deposition was performed by spinning the coater for 10 s as above (Fig.3). TiO_2 thin films then were dried at $25^{o}C$ for 15 min. The experiment was repeated to make thin films for many layers. When all the films were prepared then they were placed in furnace and temperature was gradually raised to reach annealing temperature of 200°C. Now the multilayer TiO_2 thin films are ready to analyze.



(a)



(b)

Fig. 2 (a) Stages of thin film deposition by spin coating method and (b) schematic of the Cross-section of prepared thin film.

Table I: Wet cleaning Conditions used to disinfect substrates and remove any fragments of material of oil.

Substrates	Acetone	Ethanol	DI-Water
Corning 7059 Glass	15 min	15 min	15min

Table II: Deposition Conditions of ML TiO_2 thin film growth using Sol-Gel method

PARAMETERS	RATIO	QUANTITY
Hydrochloric Acid : DI water	1:1	1 mL
Titanium Isopropoxide : Absolute ethyl Alcohol	1:8	9 mL
Final Solvent -Solution with Magnetic Stirrer time (hr)		2
Solvent-Solution Aging Time (day)		1
Annealing Time (hr) as deposition Film		2
Spun solvent-solution (ml)		0.2
Deposition Time (s)		10
Substrates		Corning 7059
Cleaning Substrates		Wet
Annealing Temperature (°C)		**RT-200**
Spin Coater rpm		11,800

D) Characterizations of the thin films

The structural properties were investigated using an XRD instrument (SIEMENS D5000 X-ray diffractometer, λ = 1.54 Å). The XRD spectra were recorded in the 2θ range from 20° to 80° at a fixed grazing angel of 5° and a scan rate of 0.02°/s. In the present study, any difference in the film thickness was corrected using the X-ray absorption coefficient for Si. Thus, the XRD intensities observed for different films can be compared. The average crystallite size, [δ], was estimated from the width of the XRD spectra using Scherrer's formula as follows:

$$[\delta] = \frac{k\lambda}{\beta\cos\theta} \qquad (1)$$

where k, λ, β and θ are a constant, the wavelength of X-ray (1.54 Å), the full width at half maximum (FWHM) and Bragg angle of the diffraction peak respectively.

The Raman spectra of the films were recorded using a portable iRaman (B&W TeK) with the argon ion laser having an excitation wavelength of 514 nm was used and the power was less than 5 mW.

The surface morphologies of ML TiO_2 films were examined by AFM (Agilent 5500 non-contact mode). The topological images were taken by scanning electron microscopy (SEM, 1450VP, Phenom Pure).

The IR absorption was measured by a Thermo Scientific, Nicolet iS10 FTIR spectroscopy with the wavenumber range of 400 to 4,000 cm^{-1} and resolution of 2 cm^{-1}.

Thickness of the films was obtained by using an ellipsometer (Rudolph Research, Ellipsometer Auto EL-III) with a wavelength of 632.8 nm.

The resistivity ρ of ML TiO_2 thin films were measured using four point probes by the following equation:

$$\rho=\frac{\pi}{ln2}\frac{V}{I}(2)$$

where v and I are voltage and current respectively.

The optical band gap energy of ML TiO_2 thin film is calculated by Tauc's equation;

$$(\alpha\ h\ \nu) = A\ (h\nu\text{-}E_g)^n(3)$$

whereh ν is photon energy and n is equal to ½ and 2 respectively. The linear variation of $(\alpha\ h\ \nu)^2$ vs hν at absorption edge. The Extrapolating the straight line portion of the plot $(\alpha h\nu)^2$ versus h ν for zero absorption coefficient values gives the optical band gap (E_g).

III. RESULTS

1) RamanAnalysis

Fig. 2 shows the Raman spectra of $MLTiO_2$thin films annealed at different temperatures in air.

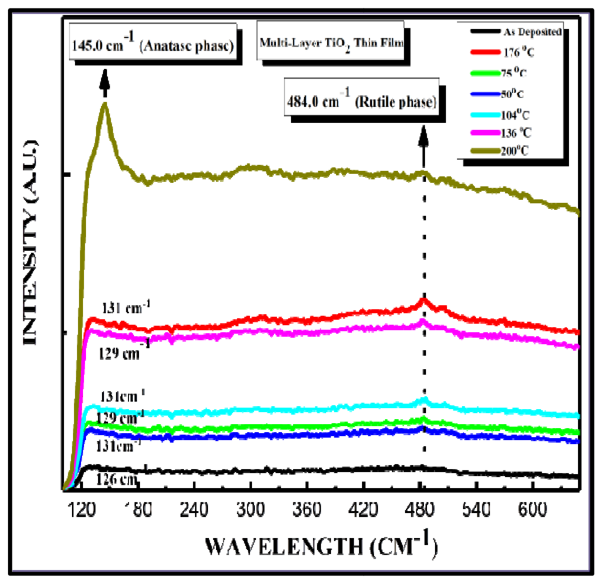


Fig. 3 Raman spectra for TiO_2 films deposited on glass substrates annealed in air for different temperatures.

The as-deposited TiO_2 films show a broad spectrum of the anatase Raman phase at 126 cm^{-1} and very weak rutile phase at 484 cm^{-1}. The spectrums at 50°C and higher temperatures, the strong anatase and rutile emission bands were formed at 145 cm^{-1} and 484 cm^{-1}, respectively. The intensities of anatase and rutile phases were found to be increased with increasing annealing temperature. However, the peak positions of anatase phases were changed from 126 cm^{-1} to 145 cm^{-1} with increasing the annealing temperature. Moreover, the peak positions of rutile phases were changed from 484.47 cm^{-1} to 482.97 cm^{-1} as shown in Fig. 4.

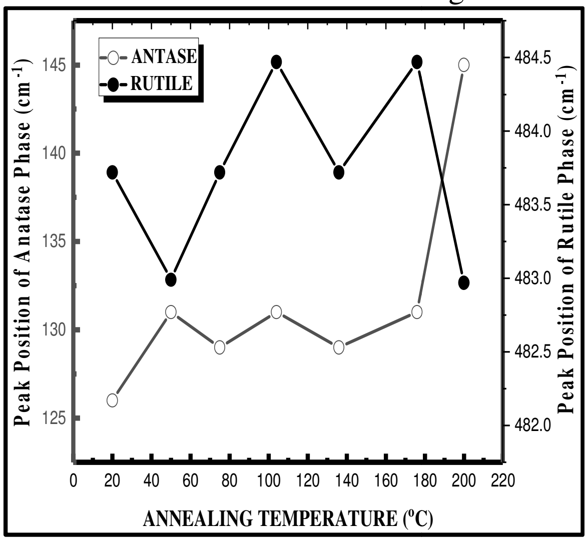


Fig. 4 Peak position of Raman spectra for TiO_2 films deposited on glass substrates annealed in air for different temperatures.

2) XRDAnalysis

Fig. 5 shows the results of x-ray diffraction for ML TiO_2 samples deposited on glass substrates as a function of annealing temperatures. As-deposited ML TiO_2films are showingvery weakcrystalline state of anatase and rutile peaks at (101), (110), (101), (004), (200), (210) and (211) orientation.

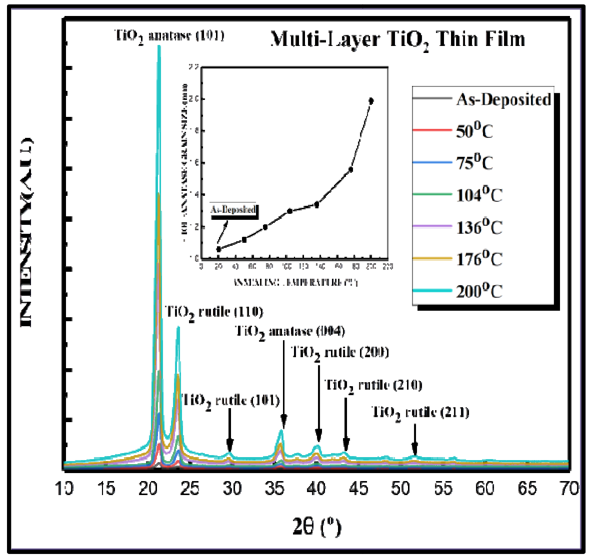


Fig. 5 XRD spectra for ML TiO_2 films annealed at different temperatures in presence of air.

At 50°C and higher temperatures, XRDintensities are found to be increased with increasing annealing temperature which is showing that the crystallinity of ML TiO_2 films is improved at higher annealing temperatures and ML TiO_2 films show the same crystalline phase in all cases. As shown in Fig. 5 (insert graph), the (101) XRD grain sizes are found to increase with increasing annealing temperature. This result is consistent with the result above.

3) FT/IRAnalysis

Fig. 6 shows the bonding properties of MLTiO_2 thin film was analyzed by FTIR in the range of 400 to 4000 cm^{-1} for as-deposited films and films annealedatdifferenttemperatures.There are significant amounts of water and carbonaceous materials are present at 3000–3700 cm^{-1} and 1300– 1800 cm^{-1} in all films.Spectrum of the as-deposited MLTiO_2 film exhibits a strong, broad absorption band at 400–800 cm^{-1}. The presence of a broad band in this region corresponds to the formation of TiO and TiO_2 bonds which isalso developingthe titanium dioxide network in the films[29-30].

The basis of peak broadening associated to the Ti-O bond might arise from the amorphous nature of TiO_2 thin film which is due to the amalgamation of carbon and/or hydroxyl groups into the Ti O bond system. With increasing the annealing temperatures, the broad band at 400–800 $cm^{-1}$are found to be sharpened with increasing intensity, corresponding to an increase in the degree of direct Ti O bonding. The content of water and its related materials in as-deposited ML TiO_2 films were diminished after high annealing temperature.

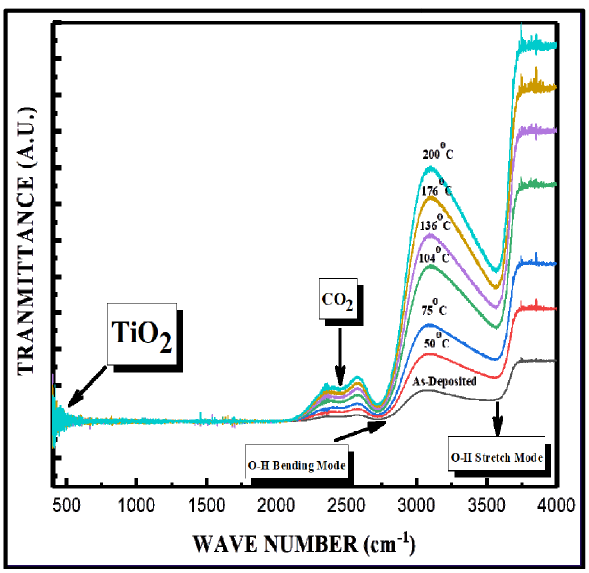


Fig. 6 FTIR spectra for ML TiO_2 films deposited on glass substrates annealed at different temperatures in Air

4) UV-visAnalysis

Fig. 7 shows the absorption spectra for ML TiO_2 thin films in the wavelength range of 200-800 nm (inner graph) and the band gap energy (E_g) with various annealing temperatures.As shown in the inner graph, there are two regions: one is strong absorption region <296 nm and other one is strong transmittance region >356 nm. All the films have almost the same absorption edges at 356 nm.

The absorption edges show the transition from valance to conduction band [31]. ML TiO_2 thin films with different annealing temperatures show the maximum transmittance (~80%) in the visible region. It is observed that a slight decrease in the transmittance for the MLTiO_2 thin films with different annealing temperatures in the UV region which is ascribed to a semiconducting nature due to the presence of band gap [32]. The optical band gap energy (E_g) of ML TiO_2 thin films as a function of different annealing temperatures is shown in Fig. 7.

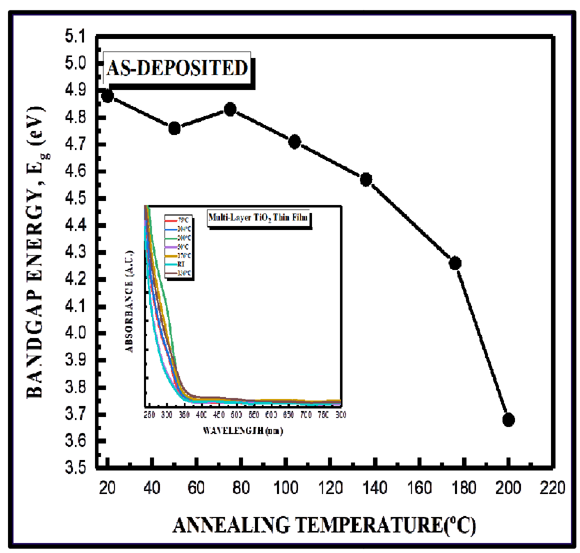


Fig. 7 Absorption spectra of ML TiO_2 thin film (Inner graph) and Band gap energy of ML TiO_2 thin Films with different annealing temperatures.

It is observed that the band gap energy (E_g)has found to be decreased from 4.88 eV to 3.68 eV as annealing temperatures increased. This decrease in the band gap energy is due to increase the grain size of ML TiO_2thin films as shown in Fig. 5. The variation of $E_g$is recommended that these films will be suitable for window material for the fabrication of high efficiency solar cells [33].

5) ResistivityAnalysis

Fig. 8 shows the variation of resistivity of ML TiO_2 thin films as a function of annealing temperature. The resistivity, ρ,of the films was calculated from the equation 2. From this figure, it is seen that the resistivity decreases with increasing theannealing temperature. The resistivity is measured for an electric field of 1MV/cm. It is observed that the as-deposited films have a resistivity of 2.5 x 10^7 Ω-m while at 200°C annealed temperature the resistivity is found to be 1.1 x 10^7Ω-m.

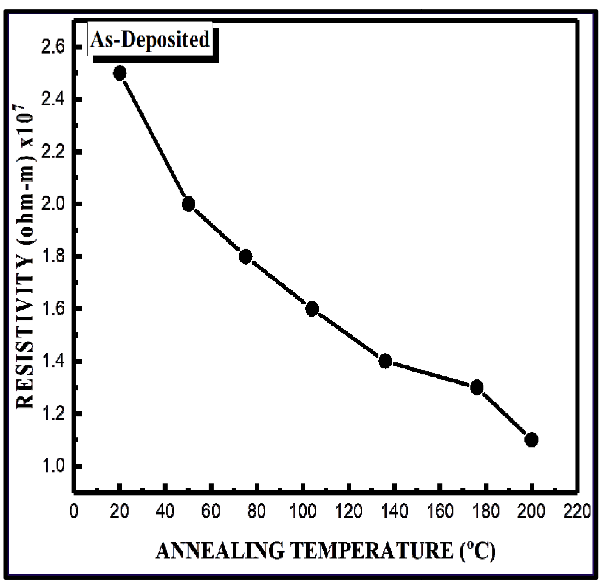


Fig. 8 Resistivity of ML TiO_2 thin films as a function of annealing temperature.

6) Dielectric constantAnalysis

Fig. 9 shows the dielectric constant of ML TiO_2 thin films as a function of annealing temperature.

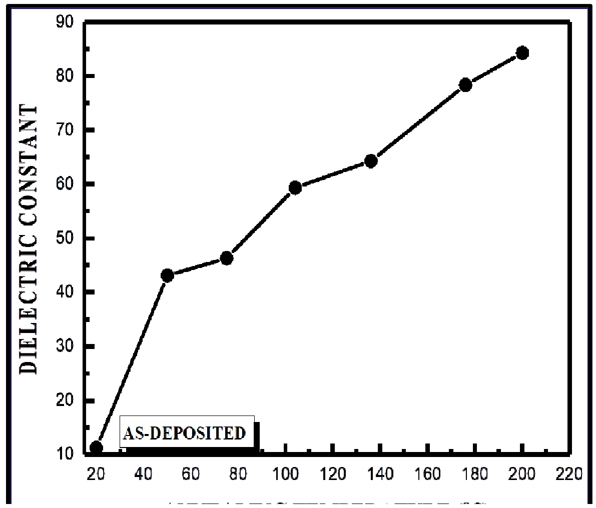


Fig. 9 Variation of dielectric constants of ML TiO_2 thin films as afunction of annealing temperature.

From this diagram, it is seen that dielectric constant of the films increased as annealing temperature increases. It varies from 11.2 to 84.3 after annealing at 200°C. The reason for this increment in dielectric constant with annealing temperature is expected to result from film densification and crystallization of minor amorphous phase in the as-deposited films that occurred during the heat treatment[34]

7) SEMAnalysis

Fig. 10 shows the SEM micrographs of ML TiO_2 thin films as a function of annealing temperatures. The SEM micrographs revealed that the surface morphology of the ML TiO_2 films depend strongly on annealing temperature. As-deposited film Fig 10a shows the agglomeration of small flaky type of structures is produced. At 50°C, the film with big flaky size is able to grow into bigger ones and prevent crack. Whereas for higher annealing temperature of 176^{o}C, it is revealed a large flaky structure with small cracks were found throughout the coatings. At 200^{o}C, it may lead to non-uniform and cracked coating and reduce coating lucidity and transparency structures were observed. It is also clearly seen that the substrate is in homogeneously covered by large flaky size and it may formed during drying process due to surface tension between the film and the air. In the case of sol-gel coated films, during drying process, the capillary forces might have generated while provides cracks on the surface.

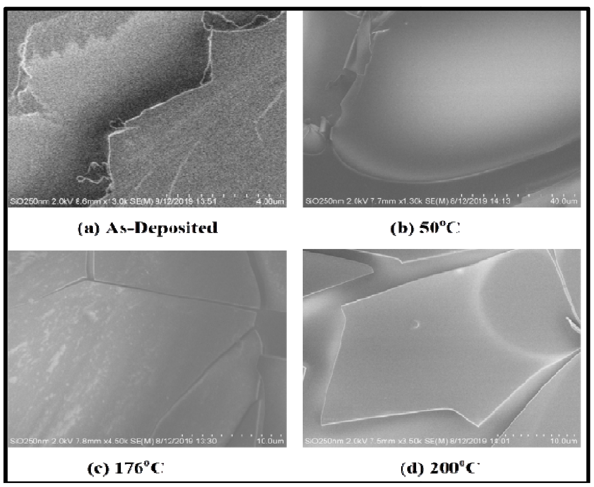


Fig. 10 SEM micrographs of ML TiO_2 thin films as a function of annealing temperatures (a) as-deposited, (b) 50^{o}C, (c) 176 ^{o}C and (d) 200^{o}C

8) AFMAnalysis

Fig. 11 shows the AFM micrographs of ML TiO_2 thin films as a function of annealing temperature(a) a-deposited, (b) 50 ^{o}C, (c) 176^{o}C and (c) 200^{o}C. The degree of surface roughness is the root mean square (rms) value of the roughness heights. The roughness of the ML TiO_2films are found to be 78.48 nm for a-deposited, 68.94 nm for 50 ^{o}C, 65.34 nm for 176^{o}Cand 50.97 nm for 200^{o}Crespectively.

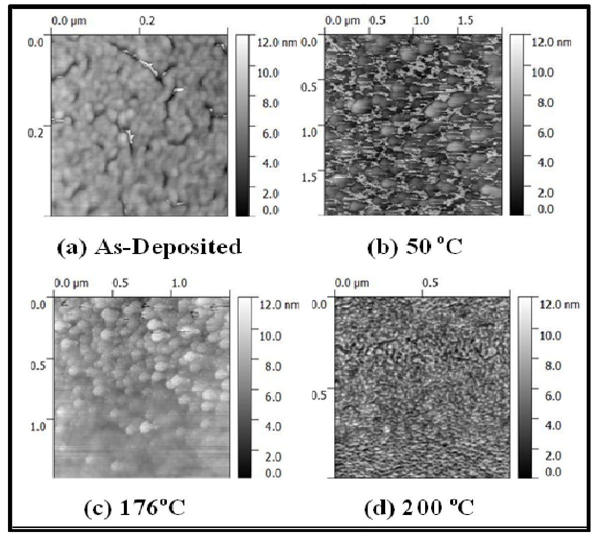


Fig. 11 AFM micrographs of $MLTiO_2$ thin films as a function of annealing temperature (a) as-deposited, (b) 50^{o}C, (c) 176^{o}C and (d) 200^{o}C

As shown in these diagrams at 200^{o}C, surface roughness is largely reduced and the roundish-like roughness having uniform heights with homogeneous grains distribution were observed. In general, the proper surface roughness is advantageous to the nucleation formation and grain growth, resulting in larger grain size in the films was obtained at higher annealing temperature. These results are well consistent with the results of Raman and XRD measurements.

VI) CONCLUSION

Titanium dioxide (TiO_2) multilayer thin films (2-layers) have been deposited successfully on glass substrate using Sol-Gel technique and annealed at different temperatures. Raman and XRD both show the weak anatase-rutile structure for the ML as-deposited films which is converted to strong structure when the films are annealed at higher temperature. XRD <101>anatase crystal structure and the grain size has been increased with increasing annealing temperature. At 200^{o}C, <101>[δ] = 20.2 nm was found. Resistivity decreased with increasing the annealing temperatureof (2.5x107 to 1.1x107 Ω-m) and UV–Vis spectroscopy which showed the high transmittance in the visible region. The optical band gap energies were found to be decreased (4.88-3.68 eV)with increasing annealing temperature which is due to the formation of sub-valence band in the forbidden band of TiO_2.In compliance to the big band gap, the thin film surface possesses a hydrophilic nature so that it could be used as anti-fogging.The dielectric constant varies from 11.2 to 84.3 for the annealed films deposited by this sol-gel process which is higher than any other conventionally produced ML TiO_2 films. Results suggested that sol-gel ML TiO_2 thin film may be a good candidate as a high permittivity insulator in thin film electroluminescent devices. As these films strongly absorb UV radiations because of the addition of layers and transmittance visible light, these might use to protect the optoelectronic devices for UV radiations.

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