Development of Electrical and Microstructure Properties in TiO_2 Thin Films: DC Reactive Method

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Abstract: ***The enhancement of electrical and microstructural properties of Titanium dioxide (TiO_2) thin films was carried out using a DC reactive method as the oxides are in the wide application of solid state devices. The method is simple and inexpensive than the other thin film fabrication methods. The tools for characterization were X-ray diffraction, SEM analysis and four probe methods. We observe the XRD peaks of present TiO_2 thin films deposited on borosilicate glass substrate at 2θ= 26.20º, 38.35º and 49.15º which were corresponding to the reflection planes (200), (220) and (311). The average size of the crystalline was also determined using Scherer formula. The structural parameters that are reflection planes, diffracted angles, full-width half maxima, lattice constants, the size of the crystal lattice and d-spacing were determined on the basis of temperature dependent. The compound analysis of EDAX spectrum provides the O/Ti ratio which was 3.19 and several phases of copper were observed in all ranges of temperatures. We conclude that an elemental composition near to stoichiometry value was observed in the films grown at 150ºC temperature.***

Keywords: ***TiO_2 films; DC reactive method; Electrical and structural properties; XRD; SEM.***

I.INTRODUCTION

Thin film Deposition technology can well be regarded as the major key to the creation of devices such as computers, microelectronic solid-state devices that were based on material structures created by the deposition techniques. Excellent stability and accuracy together with a level of reliability of the electronic components and devices was the characteristic of thin film technology. The material cost was very little as compared to the corresponding bulk material and they perform the same function when it comes into the surface processes. Thus, knowledge and determination of the nature, functions and new properties of thin films have been used for the development of new technologies for future applications. The thin film technology rapidly branching out to new industries every day. However, titanium dioxide (TiO_2) has been widely used in many applications in optical and technological fields and as a result of its innumerable advantages, among which its low cost and structural stability [1-3]. For the preparation of TiO_2-based photo-catalyst thin films, many methods was available, such as chemical bath deposition, electron beam evaporation, chemical vapor deposition, sputtering and sol-gel technique [4-6]. Among them the DC reactive sputtering method equally proved to be an efficient and versatile method to prepare TiO_2 fine thin films, allowing the control of the stoichiometry and achieve high purity and homogeneity of the thin films used in solar cells. It allows working in mild and ambient atmospheric conditions in order to obtain highly porous and nanocrystalline materials. For as much as most TiO_2 applications are limited to UV light irradiation because it only absorbs light with wavelengths shorter than 380 nm. The much research has been promoted on modification procedures to extend its spectral sensitivity to visible light, which forms the largest part of solar radiation [7]. In recent years, different approaches have been proposed to overcome this major drawback of TiO_2 films such as doping with metal ions and ion implantation [8-9]. Regardless of the innumerable works done on this subject, it was difficult to draw general conclusions on the effect of doping on TiO_2 properties. We observe a few approaches have been explored to solve the structural problems in the oxide films. Also, the TiO_2 films doped with various films have been deposited and characterized in terms of their structure and morphology properties. The number of metals such as carbon reacts elements like Au, Pt, Ag, Ni, Cu and noncarbon react elements like Ti, Mo, Nb, Cr, Zr, W etc. were used for doping into TiO_2 thin layers [10-13]. Thus, the main aim of this work is to develop DC reactive method suitable for the fabrication of TiO_2 photo-catalyst thin films.

This work mainly describes the difference between un-annealed and annealed oxide thin films behavior at various temperature. This is particularly interesting, because usually, a single preparation method is chosen, and results are reported based on the literature. TiO_2 films were prepared and studied the characteristic behavior with the variation of partial oxygen pressure in the chamber. Also, the temperature effects on coated films were understood with the morphological studies. The behavior of electrical properties for both annealed and un-annealed TiO_2 films were highlighted in the present paper. The prepared thin films were characterized by four probe method for electrical properties, XRD and SEM for structural behavior.

II.PROPOSED WORK

TiO_2 thin films were prepared in the laboratory using DC reactive sputtering method at different substrate base temperatures. The variation of the target to substrate distance and influence of O_2 pressure in the chamber is noted in the Table I. The composite films were deposited in the vacuum chamber. The titanium substrate of diameter 50.6 mm and thickness 4 mm used as such supplied from SISCO India Ltd. All the TiO_2 layers are deposited on borosilicate glass substrate (75mm X 25mm X 1.35mm) obtained from

Polar Industrial Corporation, India. Both substrates and borosilicate glasses were cleaned sequentially in an ultrasonic bath using ethanol, acetone, and de-ionized water before they were mounted on the sample holder. The schematic deposition method of the present experiment is shown in Fig. 1. The typical deposition parameters of the present study are given in Table II.

TABLE I The typical parameters in experiment.

Distance of target to substrate (mm)	*Working pressure (Pa)*
90	0.5
80	1.0
70	1.5
60	2.0

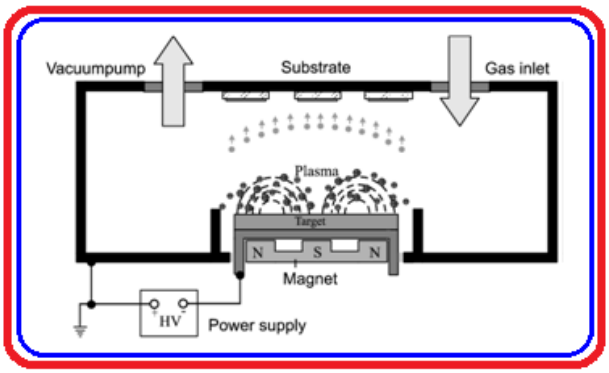

Fig. 1 Schematic diagram of the deposition system.

TABLE II: The Sputtered Parameters of TiO_2 films

Parameter	*Function*
Power system	DC voltage: -2000 V and current 3 Amps
Metal Target	Titanium purity: 99.995% Diameter: 50.8 mm Thickness: 4 mm
Substrate	Glass (75 mm x 25 mm x 1.35 mm)
Distance of Substrate (T_S)	8.0 cm
Base pressure (Torr)	$4.5x10^{-6}$
O_2 Partial Pressure (Pa)	$0.5X10^{-2}$
Substrate Temperature	373 – 523 K
Power (Watt)	40 - 80 W
Sputtering Pressure	25
Cathode current	100 – 300 nA
Cathode potential	300– 500 V
Air flow rate (SCCM)	10

In the present study, the structure and planes of elements present were discussed using X-ray spectrometer and the percent of elements as well as grain size dependence have studied by using SEM and EDAX analysis. The systematic electrical properties were discussed in detail using four-probe method with variable temperature.

III.RESULTS

The glow discharge behavior of titanium target provides the exact oxygen etch on the oxide layer to prepare TiO_2 films. The relation between cathode voltage and O_2 partial pressure was shown in Fig. 2. The cathode voltage is changed between 400 to 500 V and oxygen pressure is varied from $1X10^{-5}$ to $2.4X10^{-3}$ mbar. The sputtered power kept at 6 W cm^{-1} and rise of cathode voltage is observe while the O_2 pressure varied from $1X10^{-5}$ to $2.4X10^{-3}$ mbar. At low O_2 partial pressures the decrease in the ionization collision brings in an increase in the cathode voltage to keep up the consistent cathode current.

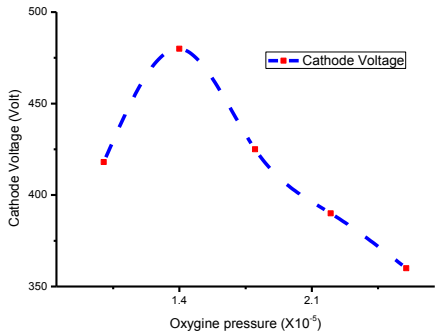

Fig. 2 Cathode voltage Vs O_2 partial pressure.

It is observed that the reduction of cathode voltage at higher O_2 partial pressure was ascribed to the oxidation of copper target. Thus, a dual nature of variation in the cathode voltage with the O_2 partial pressure was also noticed in the formation of titanium oxide films in the dc reactive sputtering [9-10].

Fig. 3 and Fig. 4 shows XRD peaks of TiO_2 thin films deposited on borosilicate glass substrate un-annealed and annealed at different temperatures. In both cases, the observed peaks at 2θ = 26.20º, 38.35º and 49.15º, were corresponding to the reflection planes (200), (220) and (311) of TiO_2 films respectively. This shows the structure of unit cell was cubic at the room temperature. There was significance structural development of thin film detected between un-annealed and annealed at various temperatures. Also, the plane (311) observed in the un-annealed is disappeared in an annealed film at room temperature [14]. The planes (220) and (211) were detected only at annealing the films at different temperatures. The variation of intensities of reflection planes were significantly detected while the temperature was varied from 100ºC to 300ºC and this is shown in figure 4. The intensities of XRD patterns increase with increase of substrate temperature changed from 100ºC to 250ºC and observed a small decrease at the temperature, 300ºC. The average size of the crystallite was also determined using Scherer formula with the peaks of XRD perpendicular to the plane. The structural parameters that are reflection planes, diffracted angles, full-width half maxima, lattice constants, the size of the crystal lattice and

d-spacing are listed in the Table 3. There was no much change of all parameters with the temperature but however the present work indicates the intensity of reflection planes with temperature.

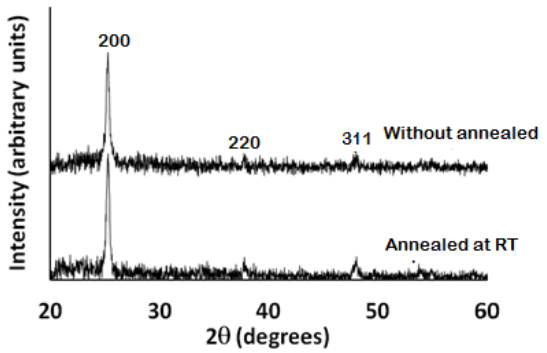

Fig. 3: XRD spectrum of TiO_2 film

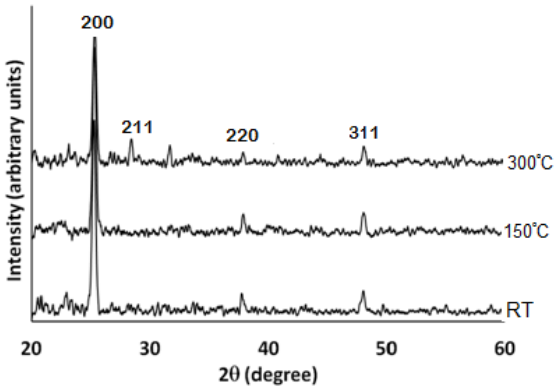

Fig. 4: Effect of temperature of TiO_2 film

TABLE III The structural parameters of TiO_2 thin films.

S.No	Substrate Temperature (ºC)	2θ (degrees)	(h k l)	d-spacing (nm)	FWHM, β (degrees)	Lattice constant, a (nm)	Crystallite Size (nm)
1.	RT	26.20	(200)	0.324	0.0625	0.584	21.45
2.	100	26.15	(200)	0.326	0.0552	0.585	22.65
3.	150	26.25	(200)	0.323	0.0651	0.584	24.35
4.	200	26.35	(200)	0.325	0.0625	0.584	26.55
5.	250	26.25	(200)	0.323	0.0654	0.582	26.95
6.	300	26.00	(200)	0.324	0.0720	0.580	27.65

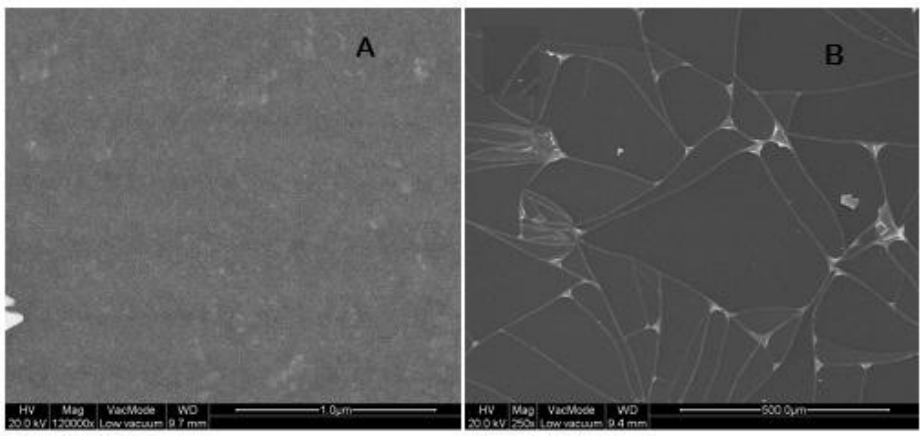

Fig. 5: SEM micrographs (A) at RT and (B) at 100ºC of TiO_2 thin films.

Fig. 5 shows the surface morphology of the TiO_2 films deposited at room temperature and 100ºC and at constant O_2 pressure, 1.0 $X10^{-4}$ Pa was kept for all temperatures. Micrographs show that no tracks in the case of un-annealed TiO_2 films and tracks were observed when temperature is 100ºC. The tracks were not modified when the temperature is above 100ºC and film phases are distributed uniformly. Also, at high temperature an enhanced tracks in the films are

due to the enhancing the oxygen partial pressure only. The EDAX spectra taken for all the samples revealed a change in the composition of Ti and O in TiO_2 films. It was observed that argon and silicon were not found along with Ti and O elements and that was absent in other layers formed at high reacting temperatures. All the films deposited at various temperatures show a similar spectrum confirming the fact that only Ti and O are present in the films. The mean ratio of Ti:O is 23.85:76.15 and an evaluated O/Ti ratio was 3.19. Thus, several phases of titanium were observed in all ranges of temperatures and an elemental composition near to stoichiometry value was observed in the films grown at 150ºC, which was also supported by XRD results studied for this investigation.

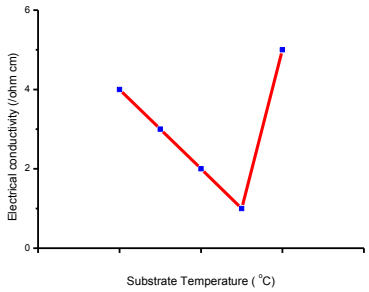

Fig. 6: Electrical conductivity Vs Temperature of the substrate of TiO_2References

TABLE IV The variations of electrical properties of TiO_2 thin films.

Substrate temperature (℃)	Electrical conductivity, σ (Ω^{-1} cm^{-1})	Thermoelectric power, S (μVK^{-1})	Carrier concentration, n (cm^{-3})	Activation energy, ΔE, (eV)
RT	$64.25X10^{-4}$	16.2	$12.25X10^{15}$	2.42
100	$42.57X10^{-4}$	21.45	$11.62X10^{15}$	2.78
150	$36.50X10^{-4}$	26.55	$12.33X10^{15}$	2.66
200	$24.28X10^{-4}$	32.05	$10.55X10^{15}$	2.62
250	$11.65X10^{-4}$	39.45	$10.05X10^{15}$	2.64
300	$6.35X10^{-4}$	42.36	$10.25X10^{15}$	2.58

The electrical transport properties of the polycrystalline thin films strongly depend on their structure [16]. The electrical conduction mechanism depends on temperature in respective of their structure of the thin films. The variation of conductivity (σ) with the temperature is according to the thermal conduction mechanism relation

$$\sigma = \sigma_o \exp(-\frac{\Delta E}{kT}) \quad (1)$$

where ΔE represent the thermal activation energy of electrical conduction, σ_o is the conductance of semiconductor material and k is Boltzmann's constant. The conductivity of thin films depends upon the temperature of the substrate is shown in Fig. 6. All the films, the conductivity has a linear function of the temperature, decreases with the increase of substrate temperature. At every temperature the linearity of the line is observed. The activation energy is determined from the slop of *ln* σ versus 1000/T (K^{-1}) plot in the higher temperature range. It is observe that the activation energy decreases with the increase of the substrate temperature and values are noted the Table IV. The decrease of ΔE was estimated with the increase of substrate temperature. The thermoelectric power measurements were determined with the formula given below.

$$s = \frac{\Delta v}{\Delta T} \mu V / K \quad (2)$$

Where ΔT is temperature gradient and Δv is thermo e.m.f at absolute temperature. The thermoelectric power is also decreases with the increase the temperature. Thus, the variations of all electrical parameters were temperature dependent and negative sign of thermoelectric power suggest that conduction should occur due to free electrons. The drop of thermoelectric power with increase of temperature indicates that the electrons are exited into conduction band, which provide transport mechanism. The positive sign indicate that the fabricated thin films are p-type semiconductor and holes are contributing the transport behavior. The active energy is also temperature dependent and more than half of the TiO_2 polycrystalline actual energy 3.14 eV. The value obtained in this process is very large than *k*T value and describe the deep level state in the forbidden state.

IV. Conclusion

The temperature effect on TiO_2 thin films electrical and structural properties were determined using DC reactive sputtering method. The significance structural development of thin film detected between un-annealed and annealed temperatures. The plane (311) observed in the un-annealed is disappeared in an annealed film at room temperature. The planes (220) and (211) were detected only at annealing the films at different temperatures along with the plane (200). The thin films deposited at various temperatures show a similar spectrum confirming the fact that only Ti and O are present in the films with the ratio of Ti:O is 23.85:76.15 and an evaluated O/Ti ratio was 3.19. The founded activation energy is more the half of its polycrystalline value and good agreement with theoretical one.

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