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Characterization of TiO_2 thin films deposited by using dc magnetron sputtering

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Abstract: Titanium dioxide thin films were deposited on silicon (111) and glass substrates by using direct current (dc) magnetron sputtering system. Thin films were deposited with different O_2 gas flow rate (1, 3, 9, 12 sccm) while keeping Ar gas flow rate constant at 30 sccm. The samples exhibit amorphous phase as deposited and become polycrystalline at 350ºC. X-ray diffraction (XRD) studies confirmed existence of anatase and rutile phase after post deposition annealing. As deposited films were transparent and their band gap increases with increase in oxygen gas flow rate. Fourier transform infrared (FTIR) spectroscopy data confirmed the existence of Ti-O band present in deposited films.

Keywords: Titanium dioxide, thin films, anatase, rutile, XRD, UV-Vis, FTIR.

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1. Introduction: Titanium dioxide (TiO_2) is a wide band gap semiconductor which has many potential applications. TiO_2, especially in thin film form, has drawn attention over the years because of its interesting optical, photocatalytic and electronic properties. Its high refractive index makes it useful in optical coatings and transparent electronics. Due to high dielectric constant and high resistivity it has drawn much attention for use in fabricating capacitors in microelectronic devices. Because of high chemical stability and modest band gap, TiO_2 thin films are widely used as photocatalysts, gas-sensing agents and as active component in dye-sensitized solar cells **[1, 2]**.

TiO_2 is known to exist in three crystalline polymorphs: rutile (R-tetragonal) (a = 4.593 Å, c = 2.959 Å), anatase (A-tetragonal) (a = 3.785 Å, c = 9.514 Å) and brookite (B-orthorhombic) (a = 5.456 Å, b = 9.182 Å, c = 5.143 Å) **[3]**. Only anatase and rutile structures are commonly observed in thin film form. Anatase is a low temperature metastable phase (<873 K) and it transforms to highly stable, rutile structure at high temperature (>1073 K) **[4]**. TiO_2 having a large band gap ranging form 3.20, 3.02 and 2.96 eV for anatase, rutile and brookite phase respectively **[5]**. The valance band of TiO_2 is composed of 2p orbitals of oxygen hybridized with the 3d orbitals of titanium **[6]**.

TiO_2 thin films can be prepared by a variety of methods such as sol–gel method **[7]**, pulsed laser deposition **[8]**, chemical vapor deposition **[9]**, spray pyrolysis **[10]** and sputtering **[11 - 13]**. In the above techniques, magnetron sputtering can produce highly uniform films with good adherence to the substrate. The method also offers the advantage of depositing films on large area substrate and offer mass scale deposition.

2. Experimental:

2.1 Instruments: Titanium dioxide (TiO_2) thin films were deposited by dc magnetron sputtering system. Deposition of thin films were done using circular titanium (Ti) target of 99.9% purity having diameter of 3 inch.

2.2 Deposition parameters and film growth: Titanium plasma were generated using dc power of 200 W and argon (Ar) gas flow of 30 sccm. Oxygen (O_2) was used as reactive gas and its concertation varied for deposition of different samples. The sputtering chamber was evacuated up to ~$1.3x10^{-6}$ Torr (base pressure) with help of turbo molecular and rotary pump. The working pressure of chamber was $5x10^{-3}$ Torr. Simultaneous deposition was made onto single side polished silicon (2x2 cm) and corning glass substrate (2.5x7 cm) of 2 mm thickness. The substrate were rotated at constant speed for uniform deposition. No substrate heating was used.

Table (1): Deposition details

Sample	Ar (sccm)	O_2 (sccm)	Base Pressure	Working Pressure	DC Power	Deposition Time
S1	30 sccm	1	~$1.3x10^{-6}$ Torr	$5x10^{-3}$ Torr	200 W	60 min
S2		3				
S3		9				
S4		12				

Table (1) shows summary of complete deposition parameters of all deposited TiO_2 films. Deposition rate vary with the variation of gas concentration and ratio. Before each deposition a pre-sputter cleaning of Ti target was done for 5 min in presence of pure Ar gas of 10 sccm. The TiO_2 thin films were grown without any external substrate heating. Post deposition annealing was performed in vacuum furnace for one hour at 350ºC. Figure (1) shows all as deposited samples with different oxygen concentration.

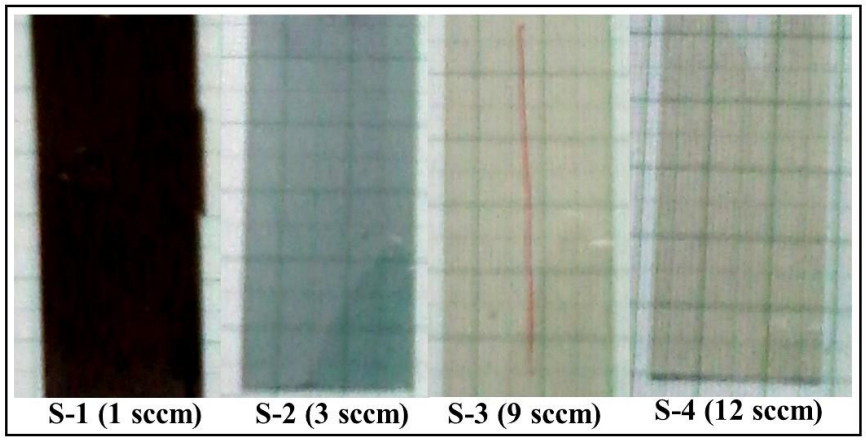

Figure (1): As deposited TiO_2 thin film samples S-1, S-2, S-3, and S-4 with respective oxygen concentration during deposition

2.3 X-ray diffraction (XRD) analysis: XRD analysis of deposited films were carried out with help of Bruker D8 Advance X-ray diffractometer by using Cu Kα (0.154 nm) radiation. The scanning was done from 20º to 100º at 2θ steps of 0.4º and scanning time 5 sec.

2.4 UV-Visible spectroscopy: The transmittance spectra (200-1000 nm) of the TiO_2 films determined using UV-Vis spectrometer (Perkin-Elmer, model Lamda-20). Optical band gap of deposited film were determined using Tauc's extrapolation method.

2.5 Fourier transform infra-red (FTIR) analysis: Optical modes and functional groups present in the deposited films were identified using FTIR where the measurement were carried out in the mid-infrared range (400-4000 cm^{-1}).

3. Results and discussion:

3.1 Deposition rate: In the present work thin films were prepared using reactive sputtering. In this process oxygen plays major role in tuning thin film properties. We changed oxygen concentrations from 1, 3, 9 and 12 sccm that affect the sputtering rate which was observed to be decreasing with increase in oxygen flow. As the deposition time was restricted to one hour, the decreasing rate leads to decrease in film thickness.

Deposition rate of samples deposited at different gas ratio was calculated by using small angle X-ray reflectometer (XRR) with Cu Kα radiation. Obtained data were fitted by keeping standard density of TiO_2 (4.23g/cm^3) (Scattering Length Density is Re = 3.4E-06 Å^{-2}, Im = 1.74E-06 Å^{-2}) and using different models with help of Parratt32 software. The XRR data of sample S-3 (thickness 25 nm) along with fitting data is shown in figure (2). That corresponds the deposition rate as 0.41 nm/min. We calculated deposition rate as well as thickness of other deposited samples by using same approach.

Deposition rate decreases and transparency increases with increase in O_2 concentration (figure (1)). However the exact correlation cannot be obtained as the thickness of the deposited TiO_2 films also varied. Deposition rate of TiO_2 film depends on several factors like – sputtering power, gas flow, substrate-to-target distance, rotation of substrate holder, substrate heating and biasing. Here we fixed the dc power, substrate-to-target distance and deposited thin films at room temperature with no substrate biasing. Hence in our case, the variation in deposition rate is due to variation in O_2 flow. The deposition rate is primarily decided by two competing factors: first the sputter rate of target with Ar gas and the rate at which the oxide layer forms on the target due to the reaction of titanium target with O_2. Sputter rate depends on the sputtering yield of the target. The yield value of metal oxides are usually lower than that of pure metal. With increasing O_2 flow, the target poisoning rate dominates which leads to decrease in deposition rate **[14]**.

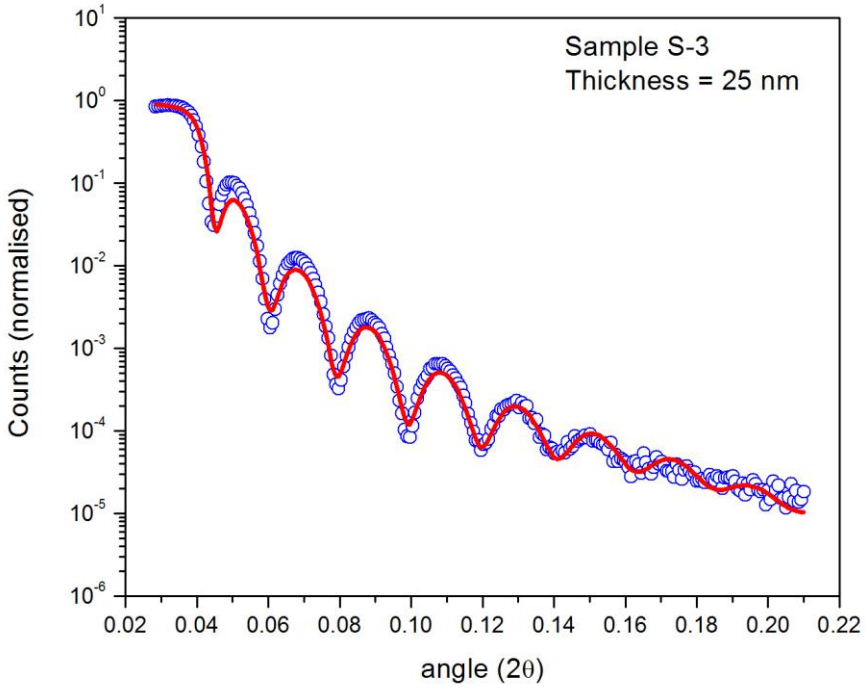

Figure (2): Calculation of thin film thickness by using XRR of sample S-3.

3.2 XRD studies: Figure (3) and (4) shows the XRD pattern of TiO_2 thin films as deposited onto glass substrate and annealed at 350ºC for 1 hour in vacuum. The as deposited samples are XRD amorphous and become polycrystalline after annealing at 350ºC. Sample S-2 (annealed at 350ºC) show both anatase (A) and rutile (R) phase **[4].** The observed peaks were at 2θ position of 25.41 (A) 38.03 (A), 48.18 (A), 54.17 (R), 55.18 (A), 62.90 (R) for 2θ. Anatase phase (101) was most prominent in the sample S-2 **[15,16]**. Brookite phase were not observed in any deposited films. Sample S-3 and S-4 were very thin (less than 25 nm thick), and are XRD amorphous.

The crystallinity of deposited films depends on the crystallinity of the substrate, substrate temperature and energy of ions. In our case, the substrates were amorphous, and kept at room temperature during deposition. These factors might have contributed to the low crystallinity of the samples. Another possible reason why as deposited films are amorphous may be found in a theory based on charged clusters **[17]**. Atoms need energy to change their structural identity either by deposition at high temperatures or by post annealing. Increase in crystallinity happen due to thermal annealing. The rearrangement of Ti and O atoms was such that the unit cell of TiO_2 tries to attain more stable and defect free configuration. Anatase and rutile are tetragonal in nature, the value of *c/a* is closer to most stable cubic lattice (c/a = 1), in case of rutile it is 0.65 and 2.51 for anatase **[18]**.

Mixed phase in TiO_2 thin films were observed by many authors. M. H. Suhail *et. al.* **[3]** deposited films by using reactive dc magnetron sputtering and reported mixed anatase and rutile phase of TiO_2. Schiller *et. al.* **[19]** by using reactive dc plasmatron sputtering, also found rutile and anatase mixture phases at substrate temperature in the range 25-500 ºC. Pawlewicz and Busch **[20]** also observed the mixed phase of anatase and rutile for substrate temperature in the range 200-500 ºC. Bange *et. al.* **[21]** and Williams *et. al.* **[22]** were observed amorphous to crystalline transition around 350-400 ºC for evaporated films and for rf sputtered films respectively. In all the cases mixed phase is present up to 600 ºC and later only rutile structure remained. Diana Mardare *et. al.* **[23]** reported mixed phase TiO_2 thin films by using dc magnetron sputtering. Ya-Qi Hou *et. al* **[15]** reported TiO_2 thin films with anatase and rutile mixed phase prepared by magnetron sputtering and annealed at 300-1000ºC. P. B. Nair *et. al.* **[24]** observed mixed phase of titanium dioxide in films prepared by rf magnetron sputtering at different working pressure and rf power. All such also confirms that the TiO_2 phase grows at higher substrate temperature and post deposition annealing.

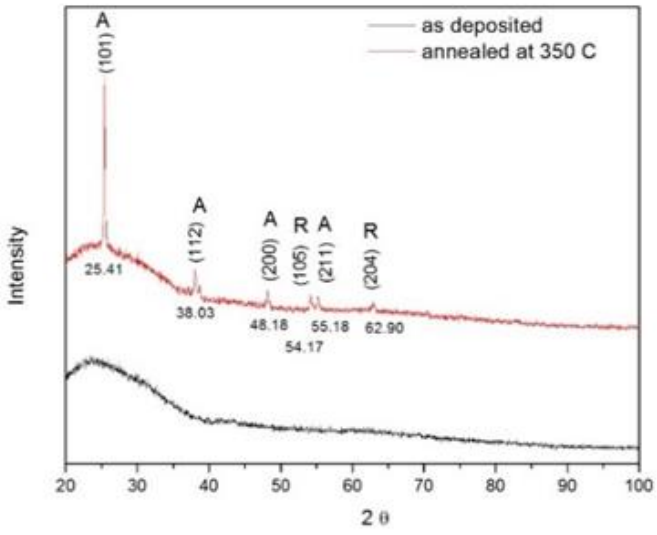

Figure (3): XRD of as deposited and annealed sample S-1.

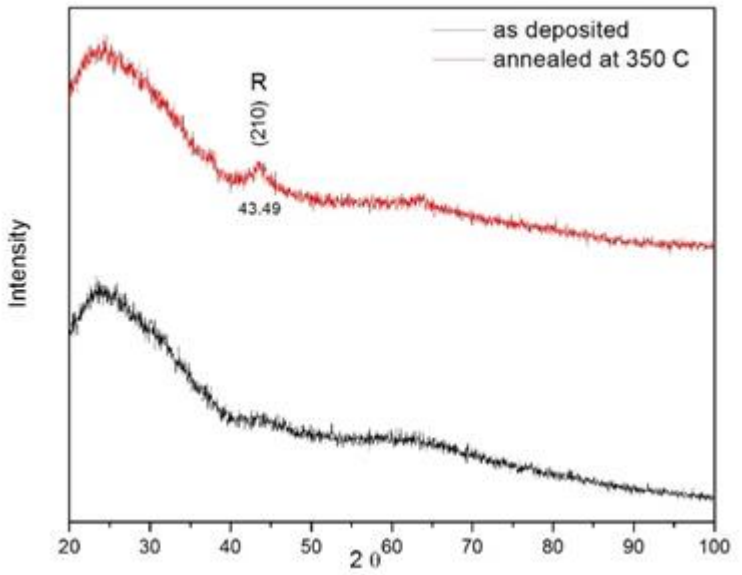

Figure (4): XRD of as deposited and annealed sample S-2.

3.3. Optical Studies:

3.3.1 UV-Visible spectroscopy: Transmittance measurement of as deposited TiO_2 thin films as a function of wavelength are shown in figure (5). Transmittance of the deposited films increases with increase in O_2 concentration. The relatively high transmittance of the film indicates its low surface roughness and good homogeneity. For $\lambda < 400$ nm, a significant fall in transmittance value is observed (figure (5)), due to the characteristic TiO_2 absorption in the UV region. The transmittance of the sample varies from 75-80 %. Ya-Qi Hou *et. al.* **[15]** reported transmittance 80-85% for films prepared by magnetron sputtering. The value of direct optical band gap was obtained by plotting $(\alpha h\upsilon)^2$ versus $h\upsilon$ (Tauc plot) in the high absorbance region. Extrapolating the linear portion of the graph to x-axis band gap (Eg) can be calculated **[25]**. Figure (6) represent the calculation of band gap by using Tauc Plot. Calculated optical energy band gap is listed in Table (2). Specimen S-1 showed no transmittance hence its band gap cannot be estimated.

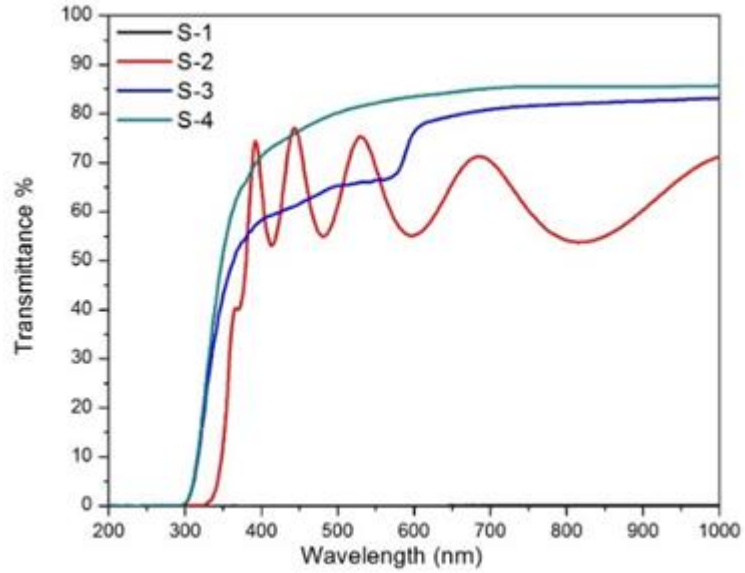

Figure (5): Transmittance of as deposited samples in UV-Visible region.

Band gaps ranging from 3.56-3.92 eV depending on processing conditions are reported in literature **[26]**. Serpone *et. al.* [**27]** have established that this can be observed in nanophase TiO_2. Optical band gap in the range 3.41–3.44 eV with increase in sputtering pressure has been reported earlier by T.M. Wang *et. al.* **[28]**. Preetam Singh *et. al.* **[29]** reported band gap of TiO_2 ranging from 3.20-3.28 eV, deposited by using dc magnetron sputtering at different sputtering pressure and power. P. B. Nair *et. al.* **[24]** reported optical band gap of TiO_2 thin films showing mixed phase ranging from 3.58-3.75 eV. We obtained band gap ranging from 3.56-3.92 eV, which is large compared to other reported band gaps. This may be due to the reduced crystallinity of the films.

Table (2): Band gap of deposited films.

Sample	S-1	S-2	S-3	S-4
Band gap (eV)	--	3.56	3.89	3.92

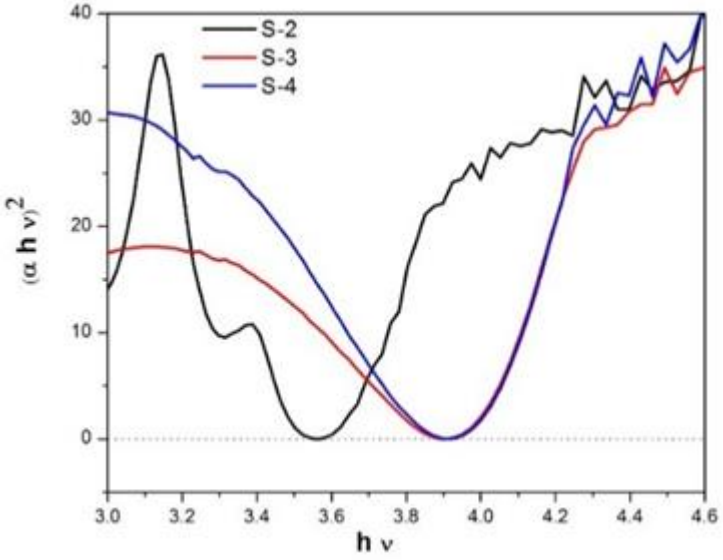

Figure (6): Band gap calculation by using Tauc formula.

3.3.2 Fourier transform infra-red (FTIR) analysis: Infrared spectroscopy were performed for all as deposited samples. Figure (7) represent the FTIR of all as deposited samples. Strong absorption was observed at 667 cm^{-1} which corresponds to Ti-O-Ti stretching vibrations and well-ordered TiO_6 octahedron. Other observed peaks are 1593 $cm^{-}1$ (C-C stretching) and 2357 cm^{-1} (O-C-O stretching). This may be due to presence of carbon and oxygen in environment. Absorption at 3645 cm^{-1} represent O-H stretching vibrations (monomer, intermolecular, intramolecular, and polymeric) and 3730 cm^{-1} is due to Si impurity present in glass substrate **[30-32]**.

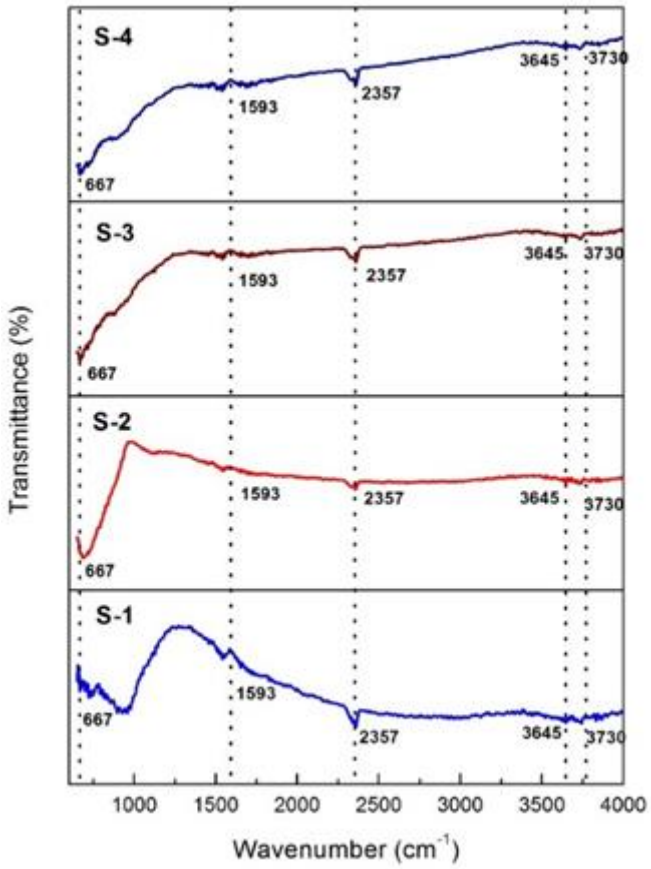

Figure (7): FTIR analysis of as deposited samples.

4 Conclusions: TiO_2 thin films were prepared with different Ar to O_2 ratio by using dc magnetron sputtering. It was observed that thickness of deposited films varies inversely and transparency is directly proportional on oxygen concentration. From XRD, we confirmed that as deposited films are amorphous. After heat treatment at 350ºC in vacuum the crystallinity of the sample gradually improved and showed mixed phase. Band gaps were calculated by using Tauc formula and optical modes were analyzed using infrared spectroscopy. The optical studies confirmed that the properties of deposited thin film are quite promising.

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