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Structural and Optical Properties of SiO_2 -TiO_2 Thin Films Synthesized by SOL-GEL Dip Coating Technique

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ABSTRACT - TiO_2 is widely used in various scientific and technological field due to its properties such as non-toxicity, chemical stability, low cost and easy preparation method. Thin films of SiO_2 -TiO_2 were deposited on to well cleaned glass substrate by using sol-gel Dip-Coating technique. The deposited films were annealing at 350°C and 450°C. The synthesized SiO_2 - TiO_2 thin films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-Visible spectroscopy (UV-Vis) and I-V characteristics. XRD analysis confirms the formation of anatase titanium dioxide and the grain size of SiO_2 - TiO_2 thin films annealed at 350°C, 400°C and 450°C were calculated as 9.31, 11.16 and 11.26 respectively. SEM images revealed the surface morphology of SiO_2 - TiO_2 with slight agglomeration. EDX analysis shows the presence of Si, Ti and O elements. UV-VIS analysis revealed the optical band gap energy of the SiO_2-TiO_2 thin films annealed at 350°C and 450°C is found it around 3.0eV and 3.07eV respectively. The current density and the electric field were measured from the I-V characteristics. When the electric field increases the current density also linearly increases and it becomes more linear at an annealing temperature of 450°C. Also the conductivity of the film was increased with decrease of resistivity at an annealing temperature of 450°C.

KEYWORDS : ***Thin films, Sol-gel method, SiO_2 - TiO_2, optical properties, structural properties***

I. INTRODUCTION

The sol-gel technique has emerged as one of the most promising new techniques for growing thin films because it has several important advantages. The major advantages of the sol-gel process are that it can be performed at low temperatures; it creates an extremely pure substrate and it is cheap to perform. Titania thin films prepared in this way can be of high purity, cost-effective and simple procedure. In this investigation, it is our interest to deposit SiO_2-TiO_2 thin films using sol-gel method. TiO_2 thin films have attracted considerable attention of use such as desensitized solar cells[1], photoelectrodes[1], photocatalyst[2,3], electrochromic displays[4], waveguides[5], gas sensors[6], resonators[7] and biomaterials[8] due to its high activity, photochemical inertness, non-toxicity and efficiency. TiO_2 is an n-type semiconductor which can be found in any of its three polymorphs: anatase(tetragonal), brookite(ortho-rhombic) and rutile (tetragonal) . TiO_2 thin films can be transformed from amorphous phase into crystalline anatase and from anatase into rutile by temperature treatment [9]. TiO_2 thin films have been synthesized using various techniques such as evaporation [10], sputtering [11,12], spray pyrolysis [13-15], sol-gel [16,17], spin coating [18,19], dip coating [20,21] and other methods. Sol-gel dip coating technique is widely used in the fabrication of TiO_2 thin films owing to its simplicity of operation, performed at low temperature, efficiency and practicality. Dip coating technique can be described as a process where the substrate to be coated is immersed in a liquid and then with drawn with a well defined withdrawal speed under controlled temperature and atmospheric conditions. The coating thickness is mainly defined by the withdrawal speed by the solid content and the viscosity of liquid. This process does not require a costly vacuum system since the coating process can be conducted under air [22]. This paper deals with the structural, compositional, surface morphology and optical properties of the SiO_2-TiO_2 thin films.

II. EXPERIMENTAL DETAIL

Titanium (IV) isoproxide (TTIP, 99%, Fluka Sigma-Aldrich) and Tetraethyl Orthosilicate (TEOS, 99%,Fluka Sigma-Aldrich) were used as starting materials. Ethanol (C_2H_5OH, 99.9%, Merck Germany) was used as a solvent. The sol-gel method was used to prepare the SiO_2-TiO_2 thin films. Firstly TEOS(Tetraethyl Orthosilicate) and TTIP (Titanium (IV) isoproxide) with fixed at 2ml where mixed into 30ml of ethonal and mixer was vigorously stirred at room temperature for 15 mins. The solution turn to pale yellowish in colour. The PH of mixed solution was adjusted to about 3-4 by 2M of HNO_3. Finally it was vigorously stirred at room temperature for 1Hour until clear sol was

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formed. Before coating, substrates were cleaned properly. The deposition condition maintained to prepare SiO_2-TiO_2 samples

Substrate	: glass
Dipping Speed	: 160.00 mm/min
Lifting Speed	: 160.00 mm/min
Length	: 20.00 mm
Wet Time	: 10 Minutes
Dry Time	: 5 minutes
Cycles	: 10 cycles
Pre- annealing time	: 30 minutes
Pre – annealing temperature	: 150^0 C
Post annealing Time	: 30 minutes
Post annealing temperature	: 350^0 C and 450^0 C

The withdrawal speed, the annealing time and temperature may vary with respect to the doping material. Finally the adhesion of the films to the substrates seems to be good.

III. RESULTS AND DISCUSSION

3.1. X RAY DIFFRACTION ANALYSIS (XRD)

X-ray diffraction patterns of SiO_2 - TiO_2 thin films at different annealing temperatures such as 350˚C, 400˚C and 450˚C were prepared by sol-gel method are shown in Fig(1) . The films are polycrystalline and fit well with the tetragonal crystal structure. The thin films have anatase phase. The diffraction peak from the XRD pattern is in agreement with the JCPDS No: 21-1272. At 350˚C , the intensity of (101) plane decreases which may be due to the decrease in the mobility of titanium and oxygen atoms which lead to the reduction in the nucleation of crystallization phase of anatase TiO_2 texture coefficient of the films which indicates abundance orientation of the crystallites along (101) plane [23]. But at an annealing temperature of 400˚C and 450˚C, the intensity of (101) plane increases gradually.

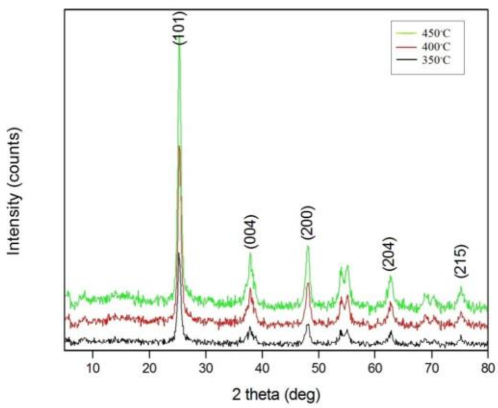

Fig (1) XRD Pattern of SiO_2 - TiO_2 thin films

The several diffraction peaks for SiO_2-TiO_2 thin films are 25.25, 37.96, 48.09, 62.81 and 75.37 and the plane values are (101), (004), (200),(204) and (215) respectively. All the diffraction peaks confirms the tetragonal anatase structure with the lattice parameters are shown in the Fig (1) correspond to main peak (101) at 2θ=25.2˚ can be well indexed to tetragonal anatase phase [24]. This indicate that the quality of SiO_2-TiO_2 film is good crystalline in nature.

3.2.SCANNING ELECTRON MICROSCOPE ANALYSIS (SEM)

Fig. 2(a) and 2(b) show the SEM images of SiO_2-TiO_2 thin films prepared at 350°C and 450°C. The SEM images revealed the homogeneous phase between the TiO_2 and SiO_2 particles. The surface morphology of the SiO_2-TiO_2 films depend strongly upon annealing temperature. It was observed that the average grain size of the films increases significantly when annealing temperature increases. At low temperatures many nucleation centers are present on the substrate and small crystals are produced. Then, the films with small crystal size are not able to grow into bigger ones. Whereas for higher annealing temperatures, the film crystal size become larger. The film annealed at 450°C has an agglomerated structure [25]. SEM images obtained from different composites indicated that the thin film thicknesses are in nanometer range.

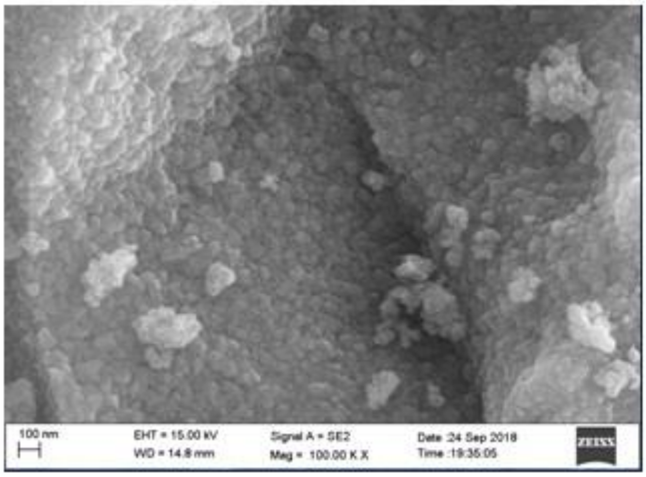

Fig. 2(a) SEM image of SiO_2-TiO_2 thin film annealed at 350°C

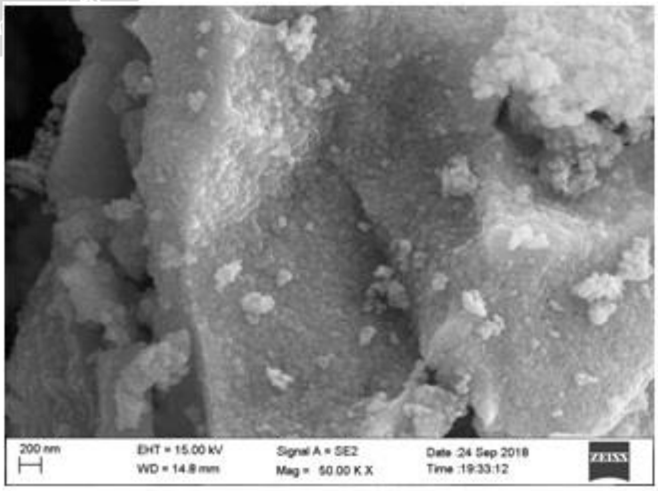

Fig. 2(b) SEM image of the SiO_2 -TiO_2 thin film annealed at 450°C

3.3. ENERGY DISPERSIVE X-RAY SPECTRA ANALYSIS (EDAX)

The micro analysis of the prepared thin film coatings were studied by Energy Dispersive X-ray Spectroscopy. Fig. 3(a) and 3(b) show that the EDAX spectra of the thin film of

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SiO_2-TiO_2 layer annealed at 350°C and 450°C respectively. TiO_2 and SiO_2 peaks were observed at both the spectrum which confirms the presence of titanium dioxide and silicon dioxide. It is observed that the mixed solution coating exhibits the regular and homogeneous surface morphology as the TiO_2 particles are covered by SiO_2 particles at the micro level.

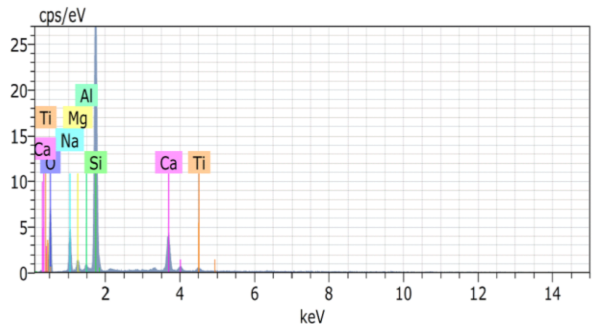

Fig. 3(a) EDAX spectra of the SiO_2-TiO_2 thin film annealed at 350°C

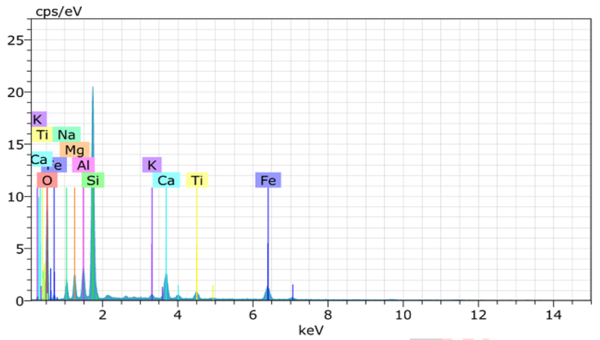

Fig. 3(b) EDAX spectra of the SiO_2- TiO_2 thin film annealed at 450°C

3.4. UV-VIS spectra analysis

Absorbance and transmittance spectra of SiO_2–TiO_2 thin films were analyzed by UV-VIS spectrophotometer. Figure 4(a) shows that the absorbance spectra of the SiO_2–TiO_2 thin film annealed at 350°C and 450°C. The absorbance spectra of the film annealed at 350°C showed higher value when compare to the film annealed at 450°C in the wavelength range of 200-250 nm. The absorption spectrum can be sensitive to surface characteristics of SiO_2 -TiO_2 thin films.

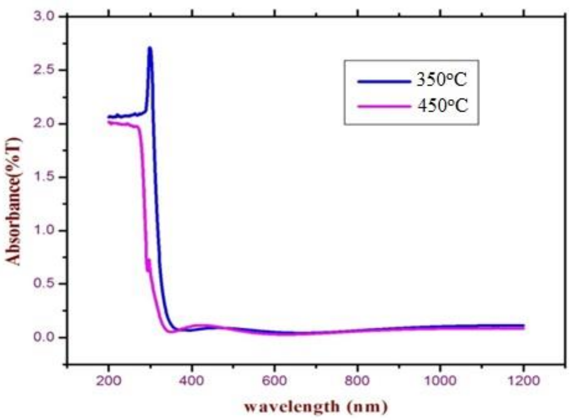

Fig. 4(a) UV-VIS absorbance spectra of the SiO_2-TiO_2 thin film

Figure 4(b) shows the transmittance spectrum of the thin film annealed at 350°C and 450°C respectively. The figure indicates the wavelength versus transmittance of SiO_2-TiO_2 thin films are transparent in the visible region and opaque in the UV region for both the annealing temperatures.

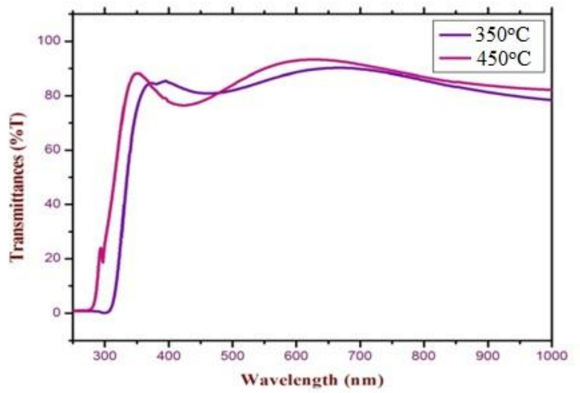

Fig. 4(b) UV-VIS transmittance spectra of the SiO_2-TiO_2 thin film

The transmittance of the SiO_2 – TiO_2 thin film annealed at 450°C is high when compared to the thin film annealed at 350°C. The Optical band gap of 350°C and 450°C SiO_2-TiO_2 thin films was calculated by using Tauc plot equation.

$$\alpha = A\,(h\nu - E_g)^{1/n}$$

α = absorption coefficient

E_g = absorption Band gap

A = constant

n = ½ for indirect band gap transition

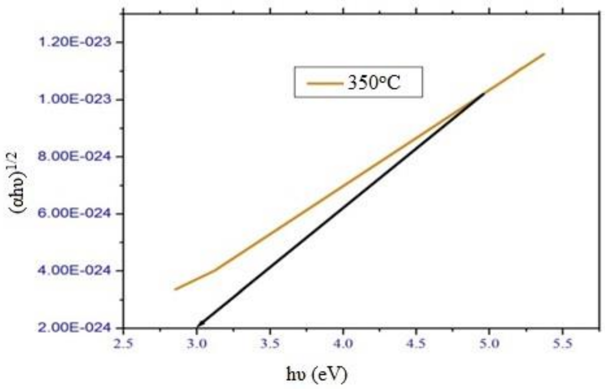

Fig. 4(c) Energy hν (eV) V_s $(\alpha h\nu)^{1/2}$ of the SiO_2-TiO_2 thin film annealed at 350°C

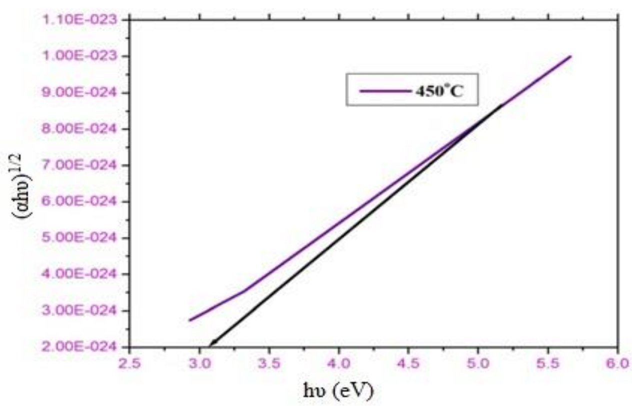

Fig. 4(d) Energy hν (eV) V_s $(\alpha h\nu)^{1/2}$ of the SiO_2-TiO_2 thin film annealed at 450°C

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Figure 4(c) and 4(d) shows that the band gap energy hυ (eV) Vs $(\alpha h\upsilon)^{1/2}$ of the SiO_2-TiO_2 thin films annealed at 350°C and 450°C respectively. The optical band gap energy of the SiO_2-TiO_2 thin films annealed at 350°C and 450°C is found it around 3.0eV and 3.07eV respectively[26].

3.5. I-V CHARACTERISTICS

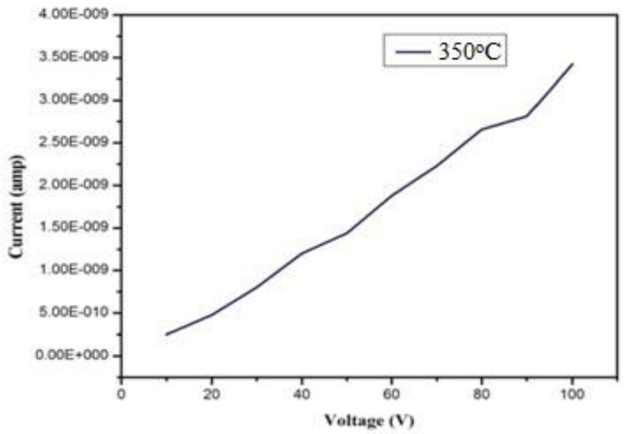

Fig. 5(a) I-V Characteristics of the SiO_2-TiO_2 thin film annealed at 350°C

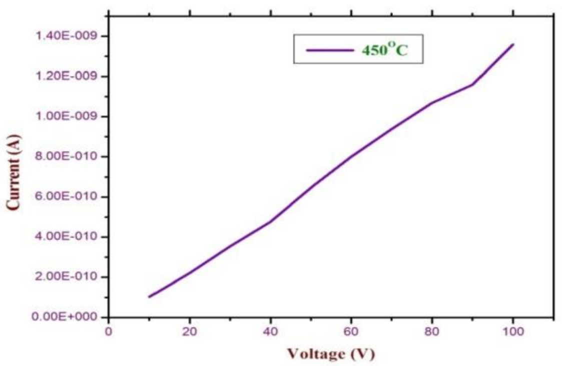

Fig. 5(b) I-V Characteristics of the SiO_2-TiO_2 thin film annealed at 450°C

Figure 5(a) and (b) shows the I-V characteristics of SiO_2-TiO_2 thin film which are annealed at temperature 350°C and 450°C for 30 minutes. The current increases with increase in voltage. It obeys Ohm's law. From these values we plot two more curves for different annealing temperatures are shown in below.

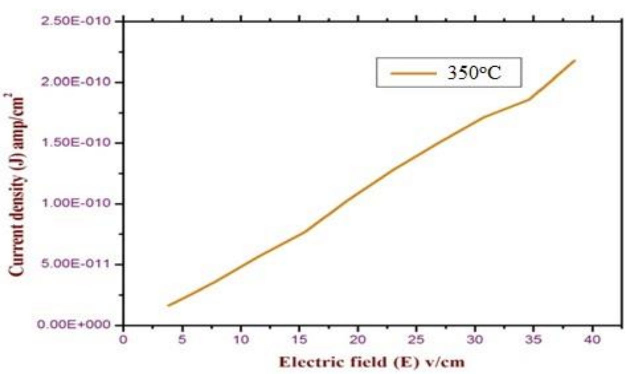

Fig. 6(a) Current density Vs Electric field of SiO_2 -TiO_2 thin film annealed at 350°C

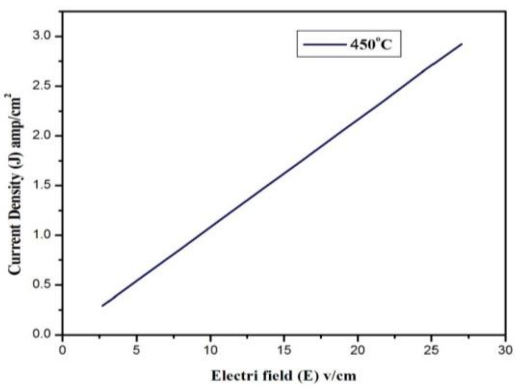

Fig. 6(b) Current density Vs Electric field of SiO_2 -TiO_2 thin film annealed at 450°C

Figure 6(a) and (b) shows the electric field Vs current density for the SiO_2-TiO_2 thin film annealed at temperature 350°C and 450°C. When the electric field increases the current density also linearly increases and it becomes more linear at an annealing temperature of 450°C. The current density and the electric field were measured from the I-V graph. The following equations are used to find the current density (J) and electric field (E).

Current density (J) = Current / Area (A/cm^2)

And Electric field (E) = Voltage / Length (V/m)

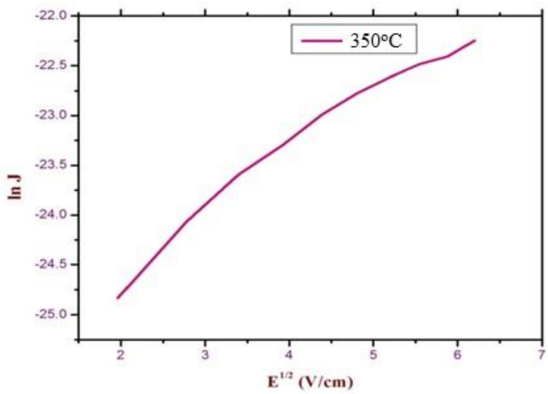

Fig. 7(a) ln J Vs $E^{1/2}$ of the SiO_2-TiO_2 thin film annealed at 350°C

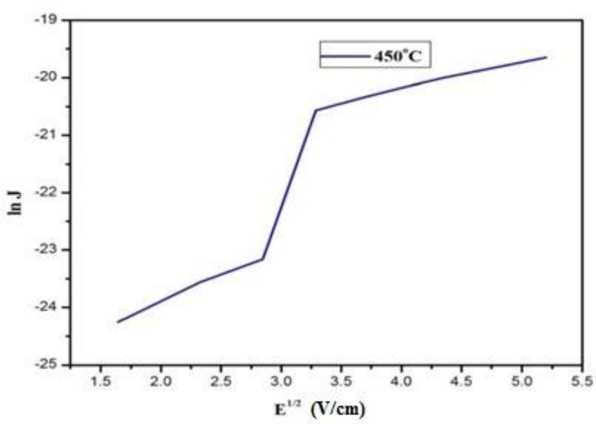

Fig. 7 (b) ln J Vs $E^{1/2}$ of the SiO_2-TiO_2 thin film annealed at 450°C

Fig.7(a) and (b) shows the relationship between ln J and $E^{1/2}$ curves of the thin film deposited on a glass substrate at an annealing temperature of 350°C and 450°C. Here we obtain a low resistance at annealing temperature of 450°C.

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This is due to grain size becomes larger, electron movement from one particle to other particle improves [27,28]. The conductivity of the film was increased with decrease of resistivity at an annealing temperature of 450°C.

IV. CONCLUSION

Thin films of SiO_2 - TiO_2 were deposited by using Sol-gel dip coating technique. The structure of the deposited films has been analyzed by X-ray diffraction technique at different annealing temperatures such as 350˚C, 400˚C and 450˚C. The films are polycrystalline and tetragonal crystal structure with anatase phase. The surface morphology of the SiO_2-TiO_2 films depend strongly upon annealing temperature. It was observed that the average grain size of the films increases significantly when annealing temperature increases. Whereas for higher annealing temperatures, the film crystal size become larger. EDAX measurements show the presence of titanium dioxide and silicon dioxide.The optical related parameters were calculated from the absorbance spectra and transmittance spectra. The absorbance spectra of the film annealed at 350°C showed higher value when compare to the film annealed at 450°C. The absorption spectrum can be sensitive to surface characteristics of SiO_2 -TiO_2 thin films. The transmittance of the SiO_2 – TiO_2 thin film annealed at 450°C is high when compared to the thin film annealed at 350°C. The optical band gap energy of the SiO_2-TiO_2 thin films annealed at 350°C and 450°C is found it around 3.0eV and 3.07eV respectively. The current density and the electric field were measured from the I-V characteristics graph. When the electric field increases the current density also linearly increases and it becomes more linear at an annealing temperature of 450°C. Also the conductivity of the film was increased with decrease of resistivity at an annealing temperature of 450°C.

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