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*Keywords:* sol-gel, conduction mechanisms, sintering temperature.

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## Electrical Conduction Mechanisms in Pure and Fe Doped Tio2 Thin Films Prepared by Sol-gel Method for Ics (integrated Circuits) Technology

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## ABSTRACT

Sol-gel dip coating was used to obtain undoped and Fe doped TiO<sub>2</sub> thin films deposited on ITO (Indium tin oxide) coated glass substrate. These films were sintered at 500 °C for 1 hour. The particle size decreases with an increase in Fe concentration. The electrical properties were analyzed by Electrometer in the voltage range -30V to +30V. We examined the various conduction mechanisms i.e. Schottky mechanism, Poole-Frenkel mechanism, ohmic and space charge limited current mechanism etc. The dominant conduction mechanism is space charge and Pool-Frenkel conduction mechanism. These conduction mechanisms depend upon the deposition parameters like sintering temperature, nature of substrate, the thickness of films, and amount of dopant.

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## I. INTRODUCTION

 $TiO_2$  is a material which has a wide range of applications such as self-cleaning of glasses, dye- sensitized solar cells, miniaturization of IC's, degradation of hazardous materials in the environment. These applications depend upon the various properties of  $TiO_2$  such as structural, photo catalytic, optical, electrical, and dielectric.

 $TiO_2$  is electrically insulating with an extremely high resistivity above  $10_8$  ohm-cm but the sub oxidized  $TiO_2$  with an excess of titanium is an n-type semiconductor with unique properties indicating the defect disorder and O/Ti stochiometry play an important role in the electrical properties of  $TiO_x$  [1].

In  $TiO_2$  thin-films the conduction processes are mainly due to hopping i.e. impurity centers while contribution of intrinsic free carriers is negligible event at high temperature. To measure the conduction current through the dielectric film we prepare the MOS structure. Incorporation of metal dopant into  $TiO_2$  changed its electrical conductivity from oxide nonconductor to oxide semiconductor with the desired p (for metal Co, Pd) and n (metal 5<sup>n</sup>, Pd) type electrical conduction due to the incorporation of metal components.

Yeo et all. Indicated the scaling limits of alternative gate dielectrics based on their direct tunneling characteristics and gate leakage requirements for future CMOS technology [2]. Various conduction mechanisms in TiO<sub>2</sub> thin films have been reported in literature includiong Poole-Frenkel [3-4], Fowler Nordheim [5] Ohmic conduction and space charge limited conductions. [6-10], Schottky Emission [11] Hopping conduction mechanism [12]. The studies of conduction mechanisms of Fe

doped  $\text{TiO}_2$  is limited. Recently the resistance switching behavior in dielectric films have been extensively studied.

In this work, we aim to examine the presence of various conduction mechanisms in pure as well as Fe doped  $TiO_2$  thin films and to correlate with the processing parameters.

#### II. EXPERIMENTAL

#### 2.1 Preparation of TiO<sub>2</sub> precursor solution

We started with 0.5M titanium butoxide solution in isopropyl alcohol. This solution was partially hydrolyzed by adding a calculated amount of water while using HNO<sub>3</sub> as catalyst for the hydrolization reaction as reported earlier [13]. The mixture was stirred vigorously with a magnetic stirrer till a clear and transparent sol was obtained. Calculated amount of iron acetyl acetonate compound, dissolved in isopropyl alcohol, was added in the TiO<sub>2</sub> solution to obtain iron doped TiO<sub>2</sub> nano-particles. Iron concentration was varied from 2 to 10-mol% in relation to TiO<sub>2</sub> to have different doping levels. All the chemicals used were of AR grade and were used as procured without further purification.

#### 2.2 Preparation of pure $TiO_2$ and Fe $/TiO_2$ films

As top Al electrodes were vacuum evaporated on the film to provide electrical contact the bottom electrode being ITO. The thickness of ITO electrode is ~ 500 nm and that of Al electrode is ~ 300 nm. Al was chosen since it has a low work function of 4.2 eV and should provide an ohmic contact with the  $TiO_2$ ; which has an electron affinity of around 4.0 eV. The value of 4.5 eV for the work function of ITO is larger than that of about an ohmic contact with  $TiO_2$  is expected to surface defects at the metal surface.

Copper wires were connected by Ag on the top electrode of film and on the ITO bottom electrode for electrical measurements. The substrates were dipped in the precursor solution and allowed to settle for two minutes before pulling out at a constant speed to obtain films of 140-160 nm thicknesses. Thin film of TiO<sub>2</sub> that formed on the ITO coated glass substrates were dried in air at room temperature, followed by drying at 100°C for 30 min in an electric oven. The films thus formed were further annealed at 500 °C for 1 h in an electric programmable furnace. The temperature of the furnace was increased at a constant rate of 3°C per minute up to the desired value of 500°C. Iron-doped titania films were prepared from Fe doped precursor solution. Iron acetylacetonate [Fe (acac) <sub>2</sub>] was used as basic material for doping TiO<sub>2</sub> precursor. Addition of iron acetylacetonate yields more homogeneous distribution of iron for each film [14]. The I-V characteristics were measured with the help of Keithley 617 programmable electrometer in the voltage range from -30V to 30 V. The ITO/TiO<sub>2</sub>/Al heterostructure was prepared by depositing the TiO<sub>2</sub> on the commercial ITO coated glass substrate and Al top electrode was fabricated by the vacuum deposition technique.

#### III. RESULTS AND DISCUSSION

#### 3.1 TEM Studies

TEM images of pure, 6 mol % and 10 mol % iron-doped  $\text{TiO}_2$  films taken at accelerating voltage of 160 KeV, are shown in figure1. The inset in figures 1(a), 1(b) and (1c) shows the electron diffraction spectra of the samples. Polycrystalline growth has been identified in all the samples, the crystallites are randomly oriented and so lattice planes, on the substrate surface. TEM studies reveal the existence of both anatase and rutile phases of  $\text{TiO}_2$  in the samples.

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*Fig.1:* (a) TEM image of Pure TiO<sub>2</sub> film





*Fig.1* ©: TEM image of 10 Fe/TiO<sub>2</sub> Film

Particles are spherical in shape in pure and iron doped  $\text{TiO}_2$  thin films. The pores of different diameters are present in all the samples. The average diameter of spherical particle is 35 nm in pure  $\text{TiO}_2$  film, while its value is 20 nm and 17 nm for 6 mol % and 10 mol % iron doped  $\text{TiO}_2$  films respectively. This indicates a decrease in particle size with increase in Fe doping concentration. The particle size decreased due to change in the surface charge and distance between the particles in the  $\text{TiO}_2$  solution. Electron diffraction (ED) patterns have been used for phase identification as shown in insets of Fig. number 1(a), 1(b) and 1(c) respectively.

From XPS studies it has been observed that titanium exists in  $Ti_{4}$  state in pure and iron doped  $TiO_2$  thin films and in iron doped  $TiO_2$  thin films iron exists in Fe<sub>3</sub> state as already reported [15].

## 3.2 Characteristics

There are two types of conduction mechanisms i.e. electrode limited conduction and bulk limited conduction. In electrode limited conduction mechanism the important parameters are effective mass of conduction carriers in the dielectric film while in case of bulk limited conduction mechanism barrier height, relaxation time, density of states, and density of interfacial states.

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Schottky emission is a conduction mechanism that if the electrons can obtain enough energy provided by thermal activation of the electrons in the metal will overcome the energy barrier at the metal dielectric interface to go to the dielectric.

As we know well, the Nordheim Fowler (FN) mechanism is associated with tunneling effect of hot carrier, The Schottky (SK) mechanism is associated with the thermionic emission across the metal insulator interface, and the Poole-Frenkel (FP) mechanism is due to the field enhanced thermal excitation of trapped electrons into the conduction band.

Fig. 2 shows the I-V curve of the MOS arrangement (Al/TiO<sub>2</sub>/ITO) hetrostructure at room temperature in the voltage range from -30 V to 30 V. I-V curves are ohmic in low field region and non-ohmic in higher field regions for all the samples. It is clear from the graph shown in figs. 2(a) and 2(b) that more than 2 mol % iron doped samples the resistance changes from LRS (Low resistance state) to HRS (high resistance state). In the ohmic region the I-V characteristics should be of the form

#### $I = (Aq\mu_P PV)/d$

Where A is the electrode area, q is the electronic charge, P is the hole current, d is the sample thickness  $\mu_{P}$  is the hole mobility.



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A typical room temperature J-V plots of pure and iron-doped  $TiO_2$  thin films is shown in fig no 2 (c). The plots of 2, 6 and 10-mol % Fe doped  $TiO_2$  films have single region which is non-ohmic. The 2 mol % Fe doped  $TiO_2$  film has two regions. Normally for space charge limited conduction, the slope in the non-ohmic region should equal to or greater than two. The value of slope is greater than 2 for pure  $TiO_2$  film while the value of slopes for Fe doped  $TiO_2$  films is less than 2 which indicates the absence of space charge conduction mechanism in Fe doped  $TiO_2$  films.

The values of slopes are smaller than those of required for space charge limited conduction. Iron acts as an acceptor impurity the dopant elements like Ca and Mg incorporated in  $TiO_2$  matrix act as an electron acceptor and decreases the electrical conductivity [16-17]. The consequence of space charge limited conduction is given by Child's law  $I=kV_2$ , Where k is constant and is taken equal to one. I and V are the current and voltage respectively.

We examined the presence of formation of Schottky barrier. A Schootky barrier is possible with an ntype semiconductor, if the work function of the metal  $\varphi_m$  is greater than the work function of semiconductor  $\varphi_s$  while it is reverse for a p-type semiconductor ( $\varphi_s > \varphi_m$ ). The work function of TiO<sub>2</sub> is 7.3 eV and the band gap is 3.2 eV. If one treats TiO<sub>2</sub> as wide band gap semiconductor, then depending on the nature of TiO<sub>2</sub> (viz. p-type or n-type), Schottky barrier may or may not be formed. Pure TiO<sub>2</sub> is reported to exhibit n-type conductivity the work function of Al metal electrode is 4.3 eV, which is lower than that of the work function of TiO<sub>2</sub>; therefore there is no possibility of Schottky mechanism (electrode limited conduction) in these samples.



A plot of log I/V Vs V<sup>1/2</sup> and log J Vs V<sup>1/2</sup> yielded approximately straight lines as shown in figs 2(e) and 2(f). These confirm that the conduction mechanism is due to Poole-Frenkel. Highest value of leakage current density is in the case of 2 mol % iron doped TiO<sub>2</sub> films. The presence of Pool-Frenkel conduction mechanism is due to the high density of traps due to this it generally occurs in thin film materials having high value of dielectric constant. In Pool Frenkel effect electrons are trapped in the localized states and due to random thermal fluctuations they will get enough energy to get out of localized state and move to the conduction band. PF emission is dependent on the concentration of trap centers (N<sub>2</sub>) and donor centres (N<sub>4</sub>). (1) When Nt< Nd then conduction mechanism is normal Pool- Frenkel emission, (2) When N<sub>1</sub>=N<sub>4</sub> then PF mechanism is called the modified PF conduction mechanism or anomalous PF effect. In such a case the slope of PF the slope is of plot is reduced by half and equal to the slope of Schottky plot. The effect of different electrode materials on the conduction characteristics is a valuable means.

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Fig. 2: (g) I Vs. (V) 2

The authors have suggested that this nonlinearity originates from a transition from field emission to thermionic emission as the applied field decreases [18]. The roughness of the films can be a factor to influence the electron transport in the junction interface of the MOSFET. With metal ion doping surface roughness of the films increases as already reported [19].

There is asymmetry of the electrical properties when the top and bottom electrodes are made of different metals. Different metals lead to different work functions and therefore results in different metal-dielectric interface. Since different types of conduction mechanisms can give rise to non linear characteristics, one can first explain observed non linearity in terms of Richardson.

Schottky or Pool-Fenkel type of conduction mechanisms. Schottky emission occurs due to thermal activation of electron over the metal oxide interface barrier because of lowering of barrier height due to the applied field. The Poole-Frenkel effect is similar to the Schottky effect except that it is applied to the thermal transfer of electrons from traps into the conduction band of the insulator. In both the cases Log I Vs. V<sub>1/2</sub> characteristics are expected to be linear in nature as shown in fig. 2 (g).

In thin-films, transport mechanisms of charge carriers is strongly influenced by particle size and which depends on the deposition parameters [20]. In order to obtain larger grains with a small number of grain boundaries, then the effect will be the decrease of carrier scattering and finally on increase in electrical conductivity.

#### IV. CONCLUSION

Pure and Fe doped  $TiO_2$  thin-films were prepared by sol-gel dip-coating method. The study of conduction mechanism through dielectric films is of great importance to the success of integrated circuits and development of switching devices and is more advantageous in comparison to conventional materials such as SiO<sub>2</sub>. The dominant conduction mechanisms are Space charge limited conduction in pure  $TiO_2$  and Pool-Frenkel conduction mechanism in pure and Fe doped  $TiO_2$  films. These conduction mechanisms are strongly dependent on the processing parameters and in general conduction mechanisms in dielectric films may be influenced by the following factors i.e. temperature, electric field, device structure, film thickness and deposition method,

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#### REFERENCES

- 1. Young Feng, Mahua Wang Yunlong Wang, Shihu Wang and Cheng Fang Fu, Advances in Condensed Matter Physics, 2013.
- 2. Y. C. Yeo, J. J. King, C. Hu, Applied Physics Letters, Vol 81, (2002), 2091.
- 3. W. Yang, J. Marino, A. Monson, C.A. Wolden, Semiconductor Science technology, 21,(2006), 1573.
- M. K. Lee, J. J. Huang, T. S. Wu, Semiconductor Science Technology, 20, (2005), 519, M. C. Sekhar, P. Kondaiah, G. M. Rao, S. V. J. Chandra, S. Uthaana, Superlattices micros- tructure, 62, (2013), 68.
- 5. Aksoy, Y. Cagliari, Journal of alloys Compounds, 613, (2014), 330,
- 6. A Bengi, U. Aydemir, S. Altindal, Y. Ozen, S. Ozilek, Journal of alloys compounds, 505, (2010), 1395.
- 7. D. Mardare, G. I Rusu, Journal of Non-Crystalline Solids, 356, (2010), 1395.
- S. Keeem, H. Y. Jeong, S. Y. Choi, Applied Physics Letters, 97, (2010), 033508, 9. L. E. Yu, S. Kim, M. K. Ryu, S. Y. Choi, IEEE 29 (2008), 331.
- 10. M. C. Sekhar, P. Kondaiah, G. M. Rao, S. V. J. Chandra, S. Uthaana, Superlattices micros- tructure, 62, (2013), 68.
- 11. H. Wobkenberg, T. IshwaraJ. Nelson, D.D.C. Bradley, S. A. Haque, T. D.
- 12. Anthapolous, Applied Physics Letters, 96, (2010), 082116.
- 13. S. D. Sharma, Davinder Singh, K. K. Saini, C. Kant, V. Sharma, S. C. Jain,
- 14. C.P.Sharma; Applied Catalysis A, 314 (2006), 40.
- J. A. Navio, Gerardo Colon, M. Macias, M. I. Litter; Applied Catalysis A; General, 177, (1999), 111.
- 16. Davinder Singh, Alka Goyal, Neenu Saini, International Journal of Scientific Research in Physics and Applied sciences, Vol 7, (2019), 35-41.
- 17. A.R. Bally, E. N. Korobeini Kova, P. E. Schmid, F. Levy, F. Bussy, Journal of Physics D: Applied Physics, Vol 31.
- 18. Mantas Scriubas, Kristina Bockute, Darious Virbukas, Giedrius Laukaitis, Procedia Engineering 98, (2014), 133-138.
- 19. E. L. Murphy and R. H. Jr. Good, Phys. Rev. 102, (1956), 1464-1473.
- 20. Marshal Dhayal, S.D. Sharma, Chander Kant, K.K. Saini, S.C. Jain; Journal of Surface Science, 602, (2008), 1149.
- 21. l. Maisel, R. Glang (Eds.) Handbook of thin film technology, Mc Graw-Hill, New York, 1970.

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