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Dielectric Properties of Sn and Fe Doped Tio_2 Thin Films Prepared By Sol-Gel Dip Coating Technique

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ABSTRACT

Dielectric properties of sol-gel dip coated Sn and Fe doped TiO_2 thin films were investigated. Dielectric constant is one of the basic electrical properties of thin films which give details about the atoms, ions and their polarization mechanism. This technique helps us to separate the real and imaginary parts of the electrical parameters and therefore provides information about the material properties. The dielectric properties of Sn and Fe doped TiO_2 thin films have been of great interest for applications in the microelectronics, microwave and telecommunication industry due to its high dielectric constant and low dielectric loss. Doping TiO_2 with Sn and Fe or other metal ions shifts the threshold for photonic excitation towards the visible range. Fe ions doped into TiO_2 have caused changes in phase composition and some properties of the catalyst such as phase composition, particle size and surface area.In this work, the electrical behaviour of the Sn and Fe doped TiO_2 thin films was studied over a range of frequency (1Hz–1MHz) and temperature (50°C & 200°C) using an impedance analyser PSM 1735 LCR Meter.

KEYWORDS : Thin films, Sol-gel method, Dielectric properties, Sn doped TiO_2 , Fe doped TiO_2.

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1. INTRODUCTION

Due to their unusually high dielectric constant, TiO_2 thin films are attractive materials for a large number of important applications such as capacitor in microelectronics, high density dynamic memory devices, microwave communication systems and telecommunication industries. As a very important functional material, the preparation, structure, performance and application of TiO_2 thin film have become many interesting physical and chemical properties. The chemical properties such as stability and non-toxicity as well as its physical properties such as high transmittance in the visible spectral region, wide band gap, high dielectric constant and dielectric loss at low frequencies[1, 2]. The dielectric constant and dielectric loss depends on the fabrication process and dielectric properties of the material. TiO_2 exists in three crystalline phases such as anatase, retile and bookie. The anatase phase has been preferred for its dielectric properties. The dielectric properties of TiO_2 have been of great interest for applications in the telecommunications industry due to its unusual high dielectric constant and low dielectric loss. The main difficulty encountered with TiO_2 is the high recombination rate of the photo excited electron hole pairs in the irradiated particles[3]. To deal with this problem, a generic way is to modify TiO_2 by doping with Tin and Iron or other metal. Doping TiO_2 with Sn and Fe or other metal ions shifts the threshold for photonic excitation towards the visible range [4]. TiO_2 thin films have been doped by many production methods including ion-assisted sputtering, plasma, ion implantation, chemical vapor deposition (CVD) and sol-gel [5]. However, a sol-gel process is considered as one of the most promising techniques due to fewer types of equipment and hence potentially lowers costs. Moreover, the most important advantage of sol-gel process over other methods is the ability to control precisely the microstructure and composition of the products [6]. During the sol-gel process, prior to gelatin, the sol could be applied as a thin film by dipping process[7]. Sol-gel technique can give a better control of particle size and homogeneity in the particle distribution [8].

This paper deals with the electrical behavior of the Sn and Fe doped TiO_2 thin films was studied over a range of frequency from 1 Hz to 1MHz at two different temperatures 50°C and 200°C using an impedance analyser PSM 1735 LCR Meter. Dielectric constant is one of the basic electrical properties of solids which give details about the atoms, ions and their polarization mechanism. This technique helps us to separate the real and imaginary parts of the electrical parameters and therefore provides information about the material properties [9,10].

2. PREPARATION PROCEDURE

2.1. *Sol preparation materials*

Titanium tetra Isopropoxide (TTIP, 97%, Sigma-Aldrich) was used as a precursor and Diethyl form amide (DMF, 99%, LOBAL) served as a solvent. Nitric acid (HNO_3, 69%, Merck) was used as a catalyst. Tin (II) chloride ($SnCl_2.2H_2O$, 98%, Merck) and Ferric Nitrate ($Fe(NO_3)_3.9H_2O$, 98%, LOBAL) was used as a doping agent.

2.2. *Preparation of Sn doped TiO_2 Sol*

20ml of N-N Dimethyl formamide (DMF) was added with 1ml of Titanium – Tetra-Isopropoxide (TTIP). After stirring for 5 minutes at ambient temperature, Tin chloride was quickly added into the solution at desired molar ratios. Two drops of HNO_3 was added five times for every 10 minutes to the above mixture. This mixture was stirred at room temperature, till we obtained a Transparent yellow solution.

2.3. Preparation of Fe Doped TiO_2 Sol

20ml of N-N Dimethyl form amide (DMF) was added with 1ml of Titanium – Tetra-Isopropoxide (TTIP). After stirring for 5 minutes at ambient temperature, Ferric nitrate was quickly added into the solution at desired molar ratios. Two drops of HNO_3 was added five times for every 10 minutes to the above mixture. This mixture was stirred at room temperature, till we obtained a Transparent brown solution.

2.4. Preparation of thin films

Doped TiO_2 thin films were obtained by the dip coating technique. In the present work, microscopic glass slides have been used as substrates. At first, substrates were cleaned in an ultrasonic cleaner with de-ionized water and then with acetone. Subsequently the well cleaned glass substrates were immersed in the sols and then dried at 150^0 C and 400^0 C for 1h. The deposition condition maintained for the preparation of Sn and Fe doped TiO_2 thin film samples are given below

Substrate	: glass
Dipping Speed	: 160.00 mm/min
Lifting Speed	: 160.00 mm/min
Length	: 18.0 mm
Wet Time	: 10 Minutes
Dry Time	: 5 minutes
Cycles	: 10 cycles
Pre- annealing time	: 1 hour
Pre – annealing temperature	: 150^0 C
Post annealing Time	: 1 hour
Post annealing temperature	: 400^0 C

The adhesion of the films to the substrates seems to be good

2.5 Dielectric characterization

Dielectric properties of Sn and Fe doped TiO_2 thin films was studied over a range of frequency from 1 Hz to 1MHz at two different temperatures 50°C and 200°C using an impedance analyser PSM 1735 LCR Meter.

3. RESULTS AND DISCUSSION

3.1. Dielectric properties of Sn doped TiO_2 thin films

The electrical behaviour of the Sn doped TiO_2 thin films was studied over a range of frequency (1Hz–1MHz) and temperature (50°C & 200°C) using an impedance analyser PSM 1735 LCR Meter. Dielectric constant is one of the basic electrical properties which give details about the atoms, ions and their polarization mechanism. This technique helps us to separate the real and imaginary parts of the electrical parameters and therefore provides information about the material properties.

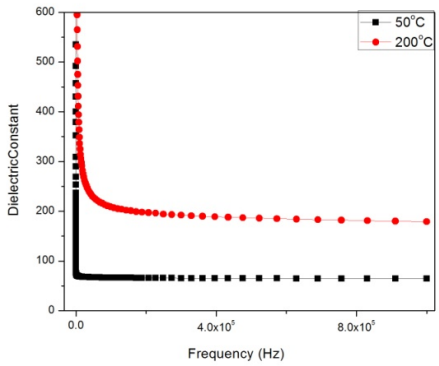


Fig (1)

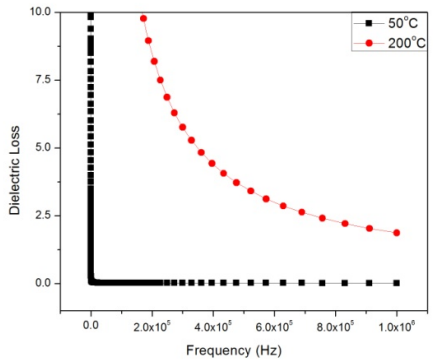


Fig (2)

Fig (1) and (2) shows variation of dielectric constant and dielectric loss with frequency at different temperatures.

The variation of relative dielectric constant and loss measured at two temperatures (50°C and 200°C) as a function of frequency (1Hz-1MHz) are shown in the Fig (1) and (2) respectively. From figure (1), it is observed that the material displays high dielectric constant at low frequencies and it becomes low when the frequency reaches to a high value. The larger value of dielectric constant at lower frequencies is due to the presence of space charge orientation, ionic and electronic polarizations [11,12,].The very low value of dielectric constant at higher frequencies is important for the fabrication of materials towards ferroelectric, photonic and electro – optic devices. The dielectric loss is also studied as a function of frequency at different temperatures and is shown in figure (2). These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric constant [13].

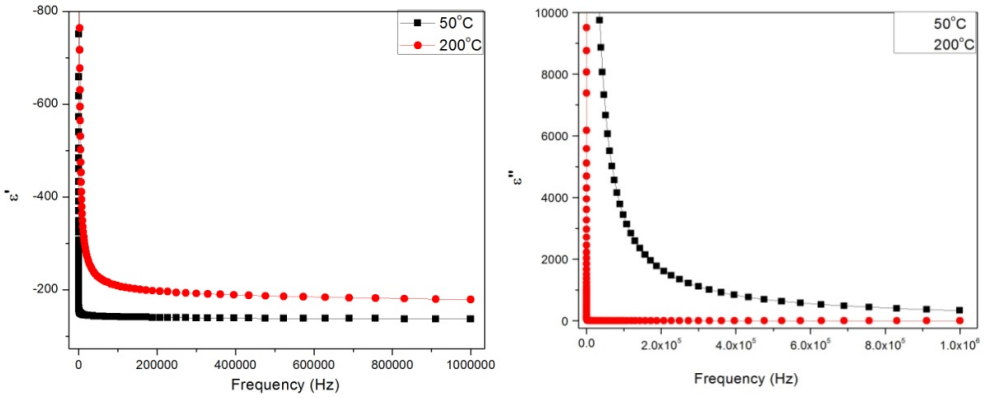


Fig (3) Frequency dependent variations of real and imaginary parts (ε′ and ε′′) at two different temperatures.

The real part of permittivity ε′ and the imaginary part of permittivity ε″ describes the energy loss of dielectrics. The absence of a dielectric loss peak in the imaginary part of the permittivity is indicative of absence of dipolar relaxation process. From the measured values of Z and θ and the sample dimensions, the real and imaginary parts of the permittivity are calculated using the relations.

$$\varepsilon' = \frac{Z''}{2\pi f c_o Z^2}$$

$$\varepsilon'' = \frac{Z'}{2\pi f c_o Z^2}$$

$$c_o = \frac{\varepsilon_o A}{d}$$

Where, ε′ and ε″ are the real and imaginary parts of complex relative permittivity, Z′ and Z″ are real and imaginary parts of impedance. c_o, ε_o, f, A and d are the geometric capacitance, the permittivity of vacuum (8.854×10−12 F m^{-1}), applied frequency, area of the sample and thickness of the sample respectively [14].

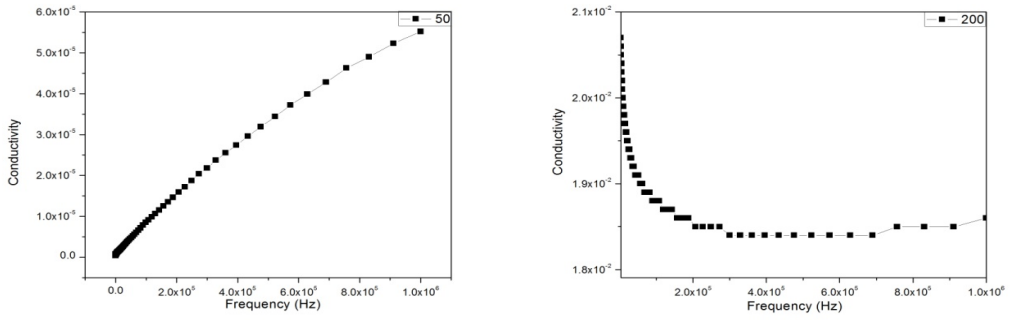


Fig (4) The variation of conductivity with respect to frequency at different temperatures.

The frequency dependence of AC conductivity, at two different temperatures for the material is shown in the above figures. The conductivity variation indicates an decrease in conductivity with rise in temperature. The electrical conductivity (σ) is calculated directly using the dielectric data and the formula is $\sigma = l/R\,A$ ohm^{-1}. Where, R is the resistance obtained for the sample, A is the area of the sample and l is the thickness of the film. It is observed that the ac conductivity increases on increasing the frequency and at high frequency, the conductivity decreases which is due to the presence of space charge polarization[15].

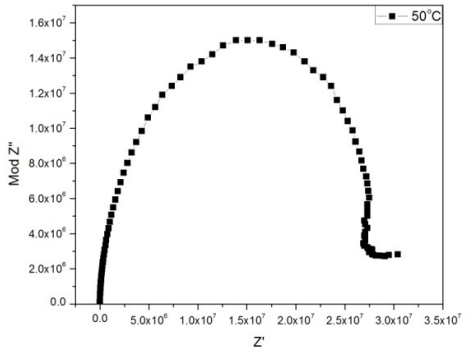
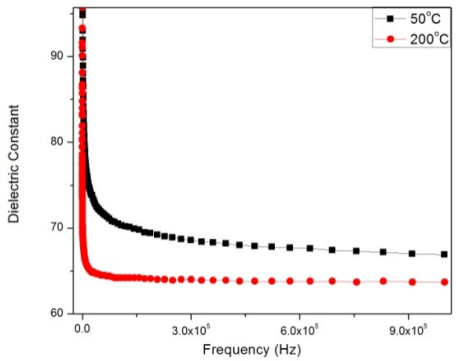


Fig (5) The complex impedance plot

Figure (4) represents the variations of the real (Z') and imaginary (Z'') parts of complex impedance as function of frequency in the form of Cole–Cole plots at 50°C temperature. Consequently, a distribution of relaxation times and decentralization of the semicircle has been observed.

3.2. Dielectric properties of Fe doped TiO_2 thin films

The electrical behaviour of the Fe doped TiO_2 thin films was studied over a range of frequency (1Hz–1MHz) and temperature (50°C & 200°C) using an impedance analyser PSM 1735 LCR Meter.



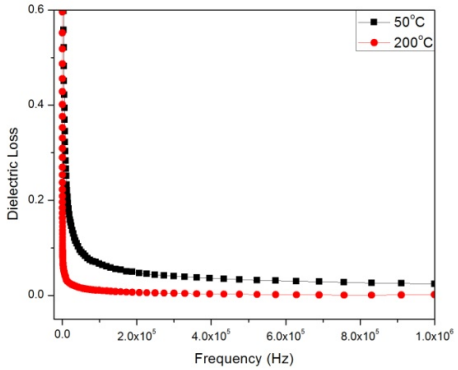


Fig (6) **Fig (7)**

Fig (6) and (7) shows variation of dielectric constant and dielectric loss with frequency at different temperatures.

The variation of relative dielectric constant and loss measured at two temperatures (50°C and 200°C) as a function of frequency (1Hz-1MHz) are shown in the Figure (6) and (7) respectively. From figure (6), it is observed that the material displays high dielectric constant at low frequencies and it becomes low when the frequency reaches to a high value. The larger value of dielectric constant at lower frequencies is due to the presence of space charge, orientation, ionic and electronic polarizations in the crystal.The very low value of dielectric constant at higher frequencies is important for the fabrication of materials towards ferroelectric, photonic and electro – optic devices. The dielectric loss is also studied as a function of frequency at different temperatures and is shown in figure (7). These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric constant[16].

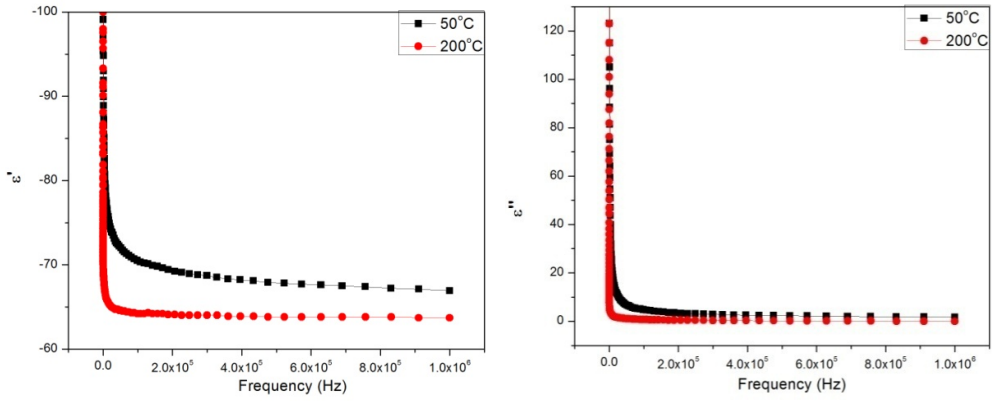


Fig (8) Frequency dependent variations of real and imaginary parts (ε′ and ε′′) at two different temperatures.

The real part of permittivity ε′ and the imaginary part of permittivity ε″ describes the energy loss of dielectrics. The absence of a dielectric loss peak in the imaginary part of the permittivity is

indicative of absence of dipolar relaxation process. The Fe doped TiO_2 thin films dielectric constant, dielectric loss, real part (ε′) and imaginary part (ε″) graphical representation curves are lower when compared to Sn doped TiO_2 thin films for both the temperatures.

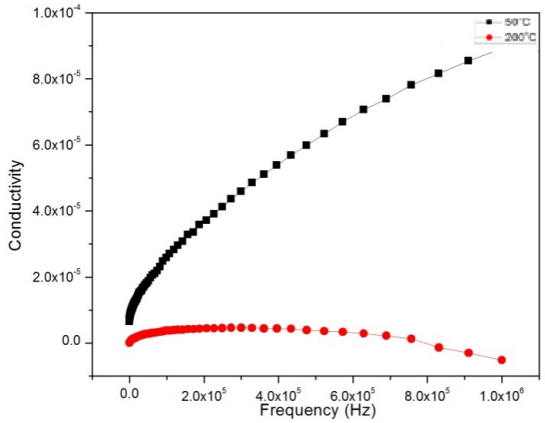


Fig (9) The variation of conductivity with respect to frequency at different temperatures.

The frequency dependence of AC conductivity, at two different temperatures for the material is shown in the above figures. The conductivity variation indicates an decrease in conductivity with rise in temperature [17]. The electrical conductivity (σ) is calculated directly using the dielectric data and the formula $\sigma = l/R\,A$ ohm^{-1}. Where, R is the resistance, A is the area of the sample and l is the thickness of the film. It is observed that the ac conductivity increases on increasing the frequency and at high frequency, the conductivity decreases which is due to the presence of space charge polarization [15].

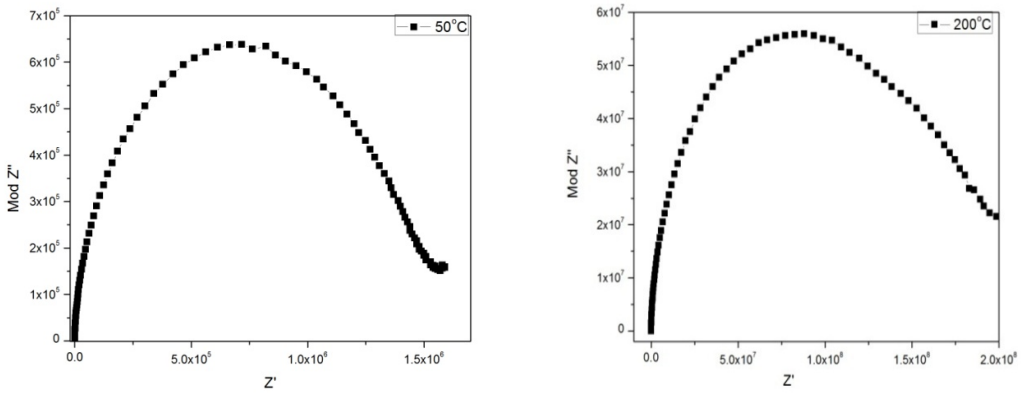


Fig (10)The complex impedance plot

Figure (10) represents the variations of the real (Z') and imaginary (Z'') parts of complex impedance as function of frequency in the form of Cole–Cole plots at two temperature. Consequently, a distribution of relaxation times and decentralization of the semicircle has been observed. Such behavior indicates poly dispersive non-Debye-type relaxation and manifests that there is a distribution of continuous or discrete relaxation time around the mean relaxation time. The semicircle in SyQuest plot shows the presence of dielectric relaxation in the film with its diameter representing the resistance of the measured sample. Single semicircular arc is present at all temperatures at higher frequency region which is due to the relaxation belonging to bulk dielectric response of the material [18,19].

4. CONCLUSION

Thin films of Sn and Fe doped TiO_2 were deposited on to well cleaned glass substrates by using sol-gel dip coating technique. Dielectric properties of Sn and Fe doped TiO_2 thin films were studied as a function of frequency at two different temperatures 50°C and 200°C. Both the material displays high dielectric constant and dielectric loss at low frequencies and it becomes low when the frequency reaches to a high value. The real part of permittivity ε′ and the imaginary part of permittivity ε″ describes the energy loss of dielectrics. The absence of a dielectric loss peak in the imaginary part of the permittivity is indicative of absence of dipolar relaxation process. The frequency dependence of AC conductivity at two different temperatures are measured. Here the AC conductivity increases on increasing the frequency and at high frequency , the conductivity decreases which is due to presence of space charge polarization. The complex impedance plot shows a distribution of relaxation times and decentralization of the semicircle has been observed. Such behavior indicates poly dispersive non-Debye-type relaxation and manifests that there is a distribution of continuous or discrete relaxation time around the mean relaxation time. The semicircle in SyQuest plot shows the presence of dielectric relaxation in the film with its diameter representing the resistance of the measured sample.

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