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Effect of the Temperature and Humidity on the Dielectric Properties of TiO_2 Thin Films Prepared by Spray Pyrolysis Technique

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ABSTRACT

The effect of the temperature and humidity on the dielectric properties such as dielectric constant and dissipation factor of the anatase phase structure of the TiO_2 film has been studied. The film has been deposited at a temperature of 350^0C using Spray Pyrolysis Technique. The structure of the deposited film has been characterized using XRD & Raman Spectroscopy. The surface morphology has been studied using SEM & EDAX. For the study of the dielectric constant and dissipation factor TiO_2 thin film has been deposited on the ITO coated glass plate.

Keywords: *Spray Pyrolysis; TiO_2, Titanium (IV) Isopropoxide, Dielectric constant, loss tangent.*

1. INTRODUCTION

Gas sensor has been remained as a subject of the extensive research over the past two decades[1]. In these applications, thin films with the higher dielectric constant are more desirable. The most commonly used oxide materials in gas sensors have been silicon oxide (SiO_2), SnO_2 [2], ZnO [3,4], Titanium dioxide (TiO_2), Indium Oxide (In_2O_3) [5] etc. The required dielectric strength and acceptable leakage current density preferably for a perfect dielectric should be greater than 3MV/cm^2 and less than 10^{-8}A/cm^2 respectively. The TiO_2 has attracted too much attention these days as both the aforementioned parameters lie within the mentioned range.

Solid state sensors with semi-insulating layer required to operate at a very higher temperature and in humid conditions. In view of this, the effect of the temperature and humidity on the dielectric constant loss tangent of the TiO_2 is very essential.

TiO_2 films have been synthesized in the literature using techniques such as spray pyrolysis [6,7], sputtering [8], Chemical Vapor Deposition (CVD) [9], dip coating method [10], pulsed laser deposition [11], sol–gel [12-16], atomic layer deposition [17] etc. Spray pyrolysis among all the aforementioned methods is quite widespread used technique due to its simplicity, commercial viability and potential for cost-effective mass production. In this method, desired titanium precursor through an atomizer onto preheated substrate is sprayed. Notable precursors are titanyl acetyl acetonate (TiAcAc) [$TiC_{10}H_{14}O_5$], Ti(i-$OC_3H_7)_4$ 2-propanol, titanium tetrachloride (TiCl4), titanium(IV) isobutoxide [$Ti((CH_3)_2CHCH_2O)$], peroxo-titanium complex solution, etc The properties of the thin film such as crystallinity, structure, morphology, growth and electrical and optical properties are dependent upon the processing conditions and precursors used. None of the paper discusses the effect of the temperature and humidity in detail on the dielectric constant and loss tangent.

In this paper, the effect of the temperature (300K to 393K) and humidity (64% to 72%) on the dielectric properties such as dielectric constant and dissipation factor of the anatase phase structure of the TiO_2 film has been studied. The film has been deposited at a temperature of 350^0C using Spray Pyrolysis Technique. The structure of the deposited film has been characterized using XRD & Raman Spectroscopy. The surface morphology has been studied using SEM & EDAX. For the study of the effect of the temperature and humidity on the dielectric properties, TiO_2 thin film has been deposited on the ITO coated glass plate.

2. EXPERIMENTS

2.1 Film Preparation

In order to deposit the TiO_2 film, TiO_2 solution has been prepared. For its preparation, Titanium (IV) Isopropoxide ($C_{12}H_{28}O_4Ti$) has been used as a source material, Acetyl Acetonate ($CH_3COCH_2COCH_3$) as a complexing agent and Absolute ethanol (C_2H_5OH) as a solvent. The prepared solutions have been taken at a volumetric ratio of 1:1.75:22.5. The films have been prepared under optimum preparation conditions [8].The substrates were cleaned before deposition and the spraying head is placed down facing the hot plate 30cm away from the substrate. The solutions were atomized with an air compressor and the compressed air pressure was maintained at 4.5

Kg/cm^2. The TiO2 films have been deposited on silicon and ITO coated glass substrate at a temperature of 350^{0}C. After preparing TiO_2 film, contact has been made using silver of diameter 0.5mm. The thickness of the film has been measured using gravimetric method and has been found to be 1μm. The thickness t of the film is given by

$$t = \frac{m_2 - m_1}{a\rho}$$

Where m_1 & m_2 are the masses of the substrates before & after deposition respectively, a is the surface area, ρ is the bulk density of TiO_2 film. The thickness t of the deposited film was found to be equal to 1μm.

2.2 Film Characterization

The structural properties of TiO2 thin films have been studied using Raman spectra (LabRAM HR controller unit) with an excitation wavelength of 514.5 nm (Ar Laser) and X-ray diffractometer (RIGAKU-MINIFLEX-II desktop) with wave length of 1.542Ǎ (Cu-Kα radiation). The surface morphology and chemical composition of the prepared TiO2 has been studied using SEM and EDAX (Ultra55 Field Emission). For the study of the dielectric constant and loss tangent, universal impedance bridge 314C has been used. The electrical resistivity and sheet resistance were determined by Van der pauw method using Keithley 2000 multimeter and Lakeshore 120 constant current (20μA). The estimated values were found to be 0.4133 Ωcm and 4.1336 KΩ/□ respectively.

3. RESULTS AND DISCUSSIONS

3.1 Structural Properties

The fig 2 shows the X-ray diffraction (XRD) pattern of TiO2 thin films. It can be seen that TiO2 has anatase phase structure as peak lies at 2θ=25.4. Fig 3 shows the Raman spectra of TiO2 thin films. It can be seen that the relative intensities of the peak is observed at wavenumber 144cm-1 and 398 cm-1. This confirms the anatase phase structure of the TiO2 film as these peaks belong to the Eg anatase modes of TiO2 films. These results match well with the result obtained in the literature [14]. The fig 4 shows the chemical composition of TiO2 thin films obtained using EDAX. The obtained atomic percentage of Oxygen to Titanium atom has been found to be 2:1 (66%:33%).

Fig 5 shows the Surface morphology of the TiO2 thin film. It can be seen that the grain boundaries are formed which may be due to the mismatch of the lattices. The grain size of the TiO_2 thin film has been found to be 1000nm.

3.2 Dielectric Studies

3.2.1 Effect of Temperature and Humidity on Dielectric constant

The relative dielectric constant of the oxide ε_{oxi} can be calculated using this relation.

$$\varepsilon_{ox} = \frac{Cd}{\varepsilon_0 A}$$

Where ε_0 is the permittivity of free space (8.85*10^{-12}f/m, and *A* (1.97*e-3m^2) is th*e* area of the contact (dot diameter is 500μm), C is the capacitance of insulator layer, d is the thickness (which is 1μm).

Fig.5 shows the dependence of the dielectric constant as a function of temperature at different frequency. It can be seen that as the temperature is increased from 300K to 307K, the dielectric constant increases first and then it starts decreasing as the temperature is increased.

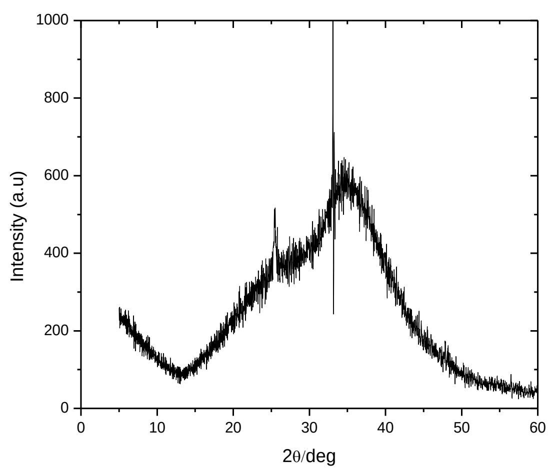

Fig 1 XRD pattern of TiO2 thin films

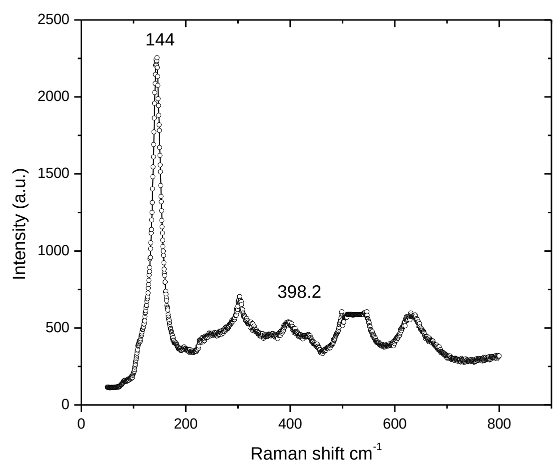

Fig 2 Raman spectra of TiO2 thin films

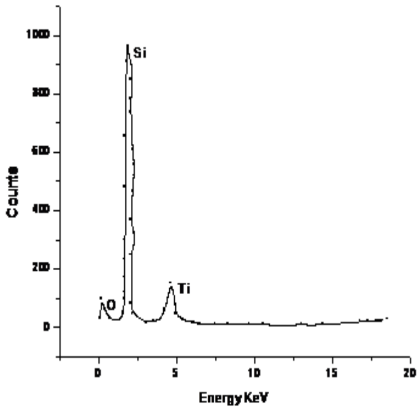

Fig 3 Energy Dispersive analysis of X-Ray

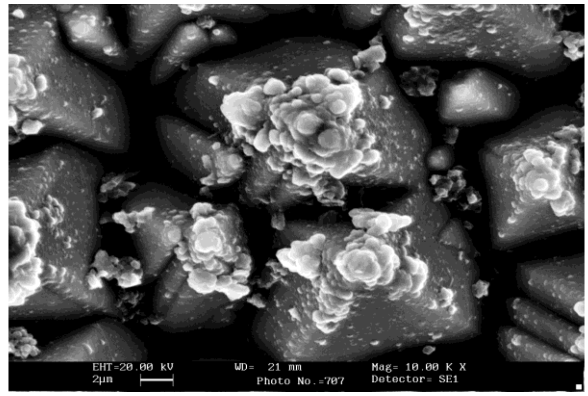

Fig 4 Surface morphology of the TiO2 thin film

The increase in the dielectric constant at low temperature is due to the dipole mechanism of the polarization as at low temperature molecules cannot orient themselves. At higher temperature, the thermal oscillations of the molecules are increased, which reduces the orderliness of their orientation. As a result the dielectric constant falls.

Fig.6 shows the dependence of the dielectric constant as a function of the relative humidity at different frequency. It can be seen that dielectric constant increases with the increase of the relative humidity. It is due to the fact that samples under consideration have large value of the porosity. Therefore, for a low value of relative humidity, the dielectric constant is low. But as molecules at higher value of humidity reduce the porosity, resultantly, the dielectric constant increases.

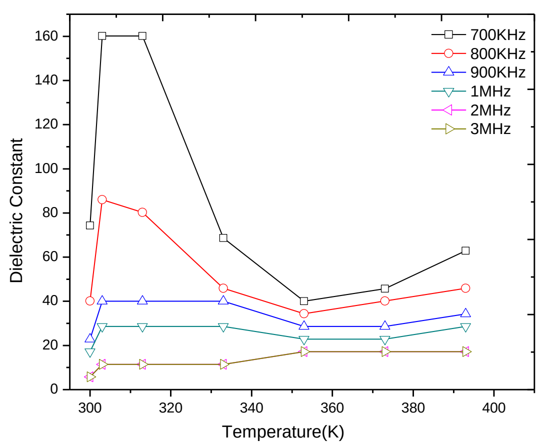

Fig.5. Dielectric constant vs temperature at different frequency

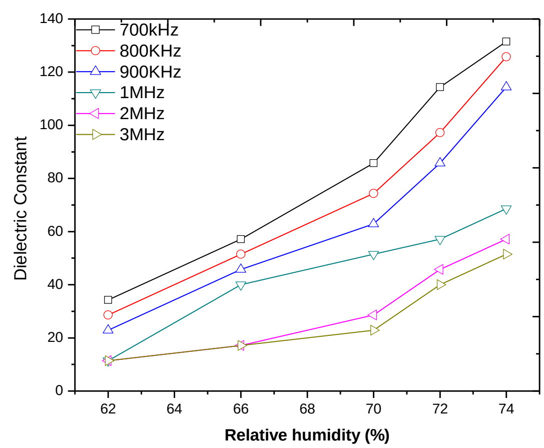

Fig.6. Dielectric constant vs relative humidity at different frequency

3.2.2 Effect of Temperature and Humidity on Loss Tangent

Dielectric losses may arise due to several causes in polar dielectrics. It is the ratio of the real part of the dielectric to the imaginary part also called as dielectric loss factor. Dielectric loss factor controls the rate at which electric energy is converted into heat in the medium. Fig.7. shows the effect of the temperature on the loss tangent at different frequencies. It can be seen that loss tangent increases initially and then it drops at a given frequency. It is due to the fact that as the temperature increases, there is a drop in the viscosity. This causes the increase in the loss due to the friction of the rotating dipoles. resultantly degree of dipole orientation increases causing increase in the loss tangent. However as the temperature is increased further, there is a reduction in the energy required to overcome the internal friction of the matter. So, it falls. The dependence of the loss tangent as a function of the frequency may show increase or decrease as it dependence upon the composition of the material.

The Fig 8 shows the loss tangent as a function of humidity at different frequencies. It has been found that at a given frequency, loss tangent decreases with the increase of the relative humidity. It is due to the fact that the water has considerable ionic conductivity. So, with the increase of the relative humidity, conduction current through the humid dielectric increases. It can also be seen that for a given relative humidity, if the frequency is increased, loss tangent decreases.

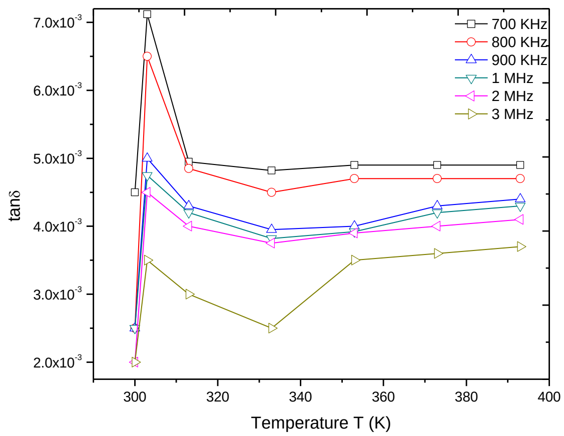

Fig.7. tanδ versus temperature at different frequency

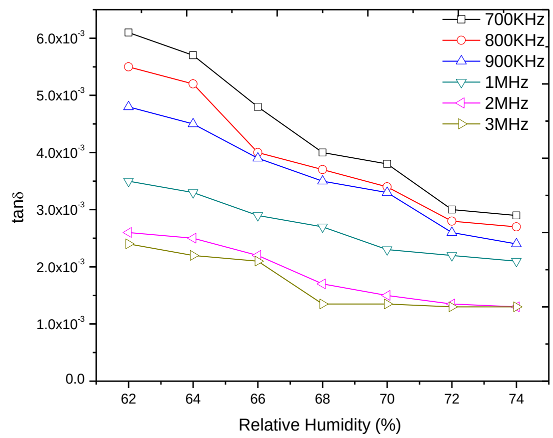

Fig.8. tanδ versus Relative humidity at different frequency

4. CONCLUSION

The influence of the temperature and humidity on the dielectric properties of the TiO_2 film has been studied at different frequencies. The TiO_2 thin film has been prepared using spray Pyrolysis technique at temperature 350^0C. The dielectric properties studied are the dielectric constant and loss tangent. It has been found that the within the temperature range under consideration, both dielectric constant and loss tangent decreases as a function of the increase in the frequency at any given temperature. The relatively higher value of the dielectric constant at low frequency is due to the interfacial polarization.

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