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Properties of thermally oxidized tin thin films deposited on alumina

S. P. Patil, Vijaya Puri*

Thick and thin film device lab, Department of Physics,
Shivaji University, Kolhapur, India.

ABSTRACT

Looking into the emerging applications of tin oxide thin films in the microwave frequency range, this paper reports the properties of tin oxide thin films of different thicknesses (103-496 nm) on alumina substrate. The tin oxide thin films were prepared by thermal oxidation (in air) of vacuum evaporated tin thin films. Surface morphology showed spherical shaped particles of tin oxide. The surface roughness was found to increase with increase in oxidation temperatures. As the oxidation temperature increases the tin oxide thin films show change from hydrophobic to hydrophilic nature. Electrical and microwave properties of tin oxide for different oxidation temperature were carried out. Microwave absorption were found to decrease with increase in oxidation temperature. Frequency and oxidation temperature dependent microwave permittivity was observed. The dielectric constant varied in the range 1.6 and 2.38.

Keywords: *Tin oxide thin film, Contact angle, Microwave absorption, Permittivity.*

INTRODUCTION

Tin oxide thin films are well known for its candidature as transparent electrodes in flat panel displays, thin film solar cells, microwave oven windows, as low emissivity glass etc. In addition to improved scratch resistance, tin oxide can also shield against radio frequency electromagnetic radiation and reduce the infrared radiation on the air conditioning system [1-2]. Good mechanical characteristics, low roughness, promoting low light dispersion and good transparency for visual light, along with blockage of infra-red and ultra-violet transmission and the recently shown ability to reflect microwave radiation [3] and use in opto-electrical devices [4] have enhanced the scope for research of tin oxide even in the microwave region. Tin oxide is a low K material. Low K is important since signal propagation velocity is a function of permittivity. The tin oxide thin films are widely studied for their properties and applications [5] but very few reports exist on the surface and microwave properties on alumina. Interfacial adhesion in low-k interconnects is a critical issue for microelectronic devices. Tin oxide thin film has been reported to have high adhesion [6]. Low-dielectric constant material is required for the interconnect structure to reduce propagation delays, cross-talk noise between metallization, and power dissipation. Strong efforts are being invested to find a suitable insulator material with a dielectric constant below 3.0. Alumina being a very popular substrate for high frequency applications, the study of low K materials on alumina may prove useful. Tin oxide thin film can be prepared by a number of methods [7-10].

In the present paper, tin oxide thin films have been obtained by thermal oxidation (in air) at various oxidation temperatures of vacuum evaporated tin thin film on alumina. The contact angle of the tin oxide thin film on alumina was studied. The variation of X band (8-12 GHz) electromagnetic absorption of the tin oxide thin film due to

thickness and oxidation temperature were also investigated. Frequency and thickness dependent electromagnetic permittivity is also presented in this paper. Reports on microwave properties of tin oxide thin film are very sparse and those available are on glass substrate.

MATERIALS AND METHODS

Pure (99.7%) metallic tin was used as the source material for the evaporation of tin thin film on alumina substrate. Tin thin films of various thicknesses (113nm, 206nm, 309nm and 511nm) were deposited by resistive heating under a vacuum of 5 x 10^{-5} mbar using a molybdenum boat. After the deposition, the tin thin films were oxidized in air atmosphere at different temperature of 160^0**C**, 200^0**C**, 250^0**C** and 300^{0}C for 10 minutes. The thickness of the tin oxide thin film was 103nm, 198nm, 304nm and 496nm. Thickness of tin and tin oxide thin films was measured by XP-1 surface profiler (AMBIOS Technology) and contact angle by using contact angle goniometer (Ramehart instruments company USA). X-ray diffraction analysis was performed by a Philips (PW 3710) diffractometer. The surface morphological study was carried out by scanning electron microscopy (JSM- 6360 JEOL, Japan). Electromagnetic absorption was studied in the X-band (8-12 GHz) using waveguide reflectometer set-up [11]. The permittivity of tin oxide thin films at microwave frequency was measured by using Voltage Standing Wave Ratio (VSWR) slotted section method [12]. The measurement of the perturbation in the position of the maxima and minima gives the permittivity of the medium. The real and imaginary part of the permittivity was calculated by using Smith chart.

RESULTS AND DISCUSSION

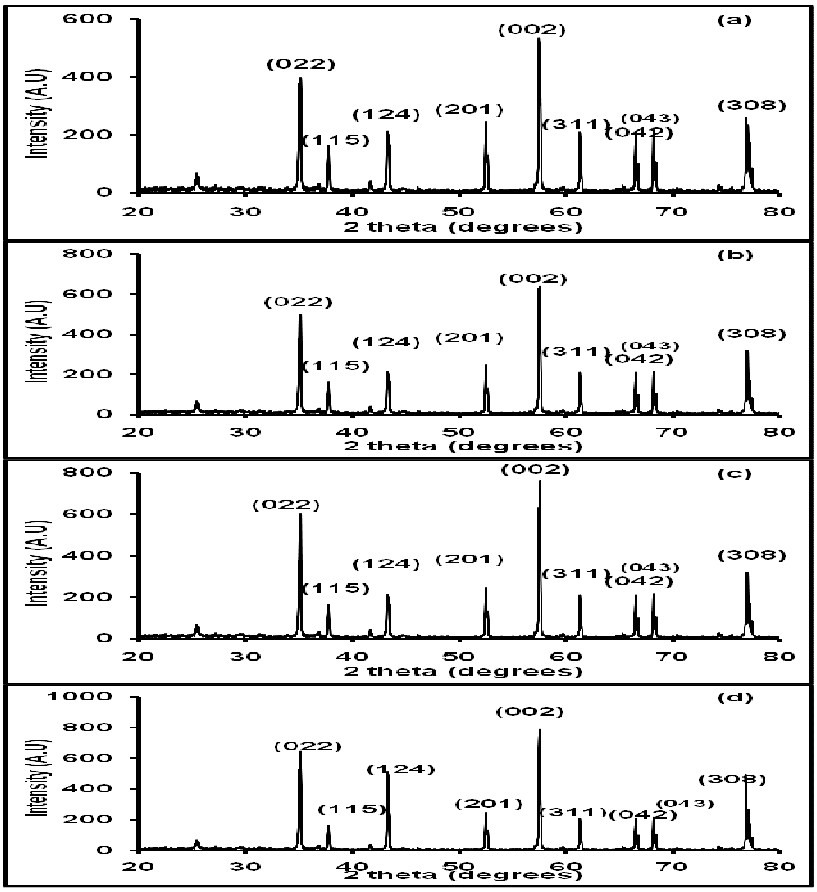

Fig.1: XRD pattern of tin oxide thin film for different oxidation temperatures on alumina (a=160^{0}C, b=200^{0}C, c=250^{0}C and d=300^{0}C)

Figure 1 shows the XRD pattern of tin oxide thin film. XRD patterns observed at all the oxidation temperatures (1600, 2000, 2500 and 3000C) were almost similar. No evidence of tin was observed indicating complete oxidation of tin to tin oxide. The X-ray diffraction pattern of tin oxide thin film showed the tetragonal structure with dominant (002) plane, mixed with orthorhombic phase with dominant (022) plane.

Alumina is highly crystalline. Film thickness is so small that X-ray easily reach the substrate and hence material orient the direction of alumina. So peaks of alumina (substrate) were overlapped by tin oxide peaks. For all the temperatures, both the tetragonal and orthorhombic phases of tin oxide were observed. The orthorhombic phase has been reported by other workers on glass [6, 13-15]. The existence of SnO was observed on glass substrate (deposited by the same method as used here) [8, 15] whereas it is absent on alumina substrate, indicating a more stable structure of tin oxide on alumina as compared to glass substrate. Totally different phases of tin oxide have been observed on alumina as compared with those on glass substrate [8, 15]. All the peaks are sharp indicating the films oxidized are polycrystalline in nature. The substrate and impurity peaks are absent. As temperature increases the tin oxide thin films becomes more crystalline. Due to heating, mobility of adatoms as well as nucleation site increases and elimination of trapped excess vacancies occur which results in increased thin film crystallinity. It was observed that, the crystallinity of tin oxide thin films showed improvement with increase in oxidation duration. The crystallite size of tin oxide thin film was calculated using Scherrer's formula [16]. The crystallite size of tin oxide thin film for oxidation temperature 160^0C was 52 nm. The crystallite size was found to increase up to 52.92 nm with increase in oxidation temperature.

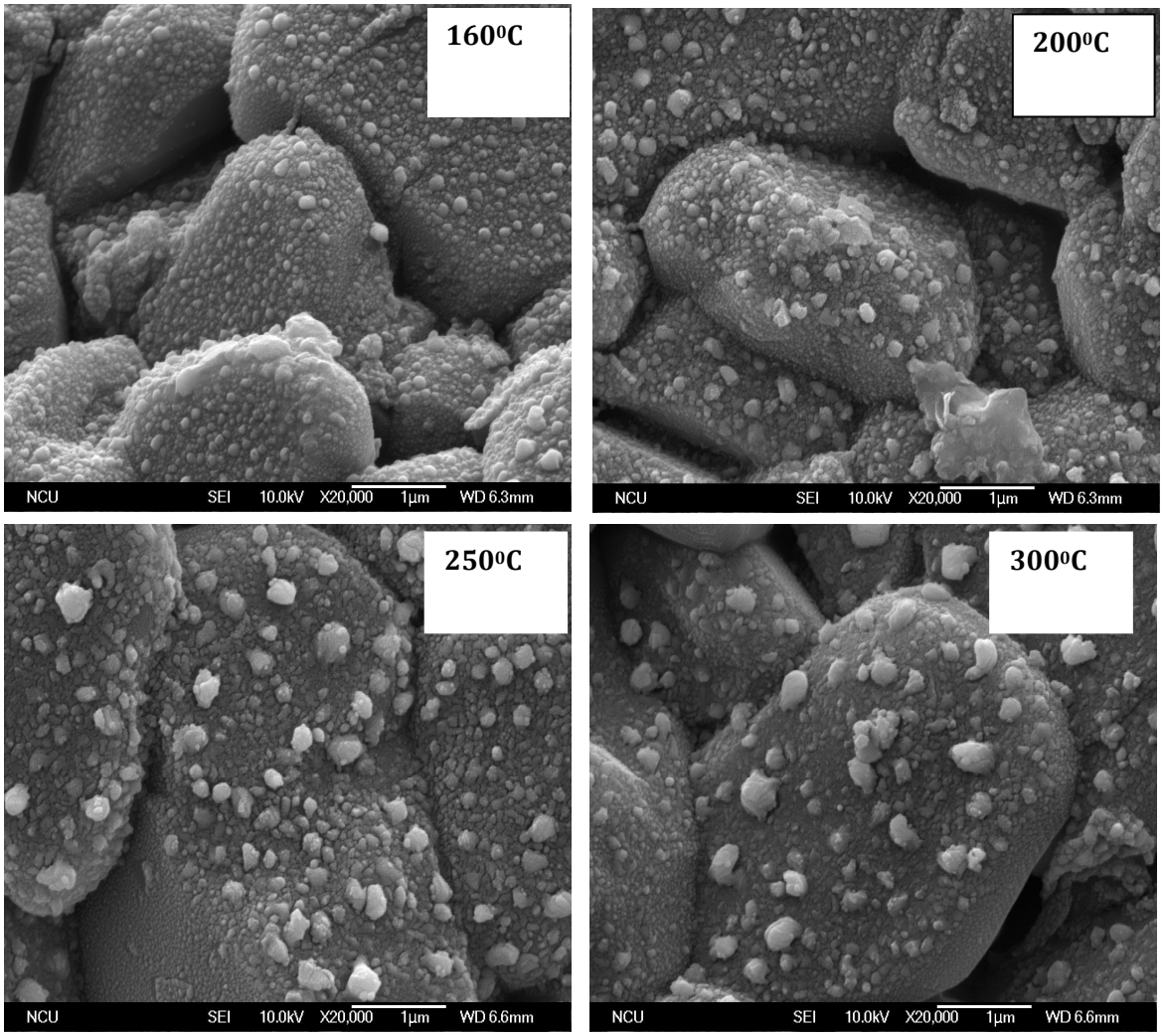

Fig. 2. SEM images of tin oxide thin film for different oxidation temperatures

Surface morphology

Scanning electron microscope (SEM) images of tin oxide thin film oxidized at different oxidation temperatures is shown in figure 2. The tin oxide thin film showed spherical shaped grains. SEM image of tin oxide thin film on alumina showed grains of alumina also and on that tin oxide.

From the figure it is seen that the tin oxide thin film shows compact surface morphology with non uniform grains. It is known that vacuum deposited films at lower substrate temperatures have very small grain sizes while those deposited at higher substrate temperature have larger grain sizes. This could be due to an enlargement of the grains and indicating improvement of the crystal quality with increasing temperature. Grain size of tin oxide particles was increased and clearly seen from SEM image. The grain size of tin oxide thin film was 180nm. Appearance of new grain growth is observed as oxidation temperature increases. As oxidation temperature increased the grain size of tin oxide thin film increased and it was 280nm.

The surface morphology of the deposited thin films depends on the thin film growth. In this paper meal thin film were deposited by vacuum evaporation technique and after deposition oxidation was done. So the oxidation temperature also plays a vital role in surface morphology modification. During the thin film growth there are two steps, the first step aims to form a seed layer on the substrate by the formation of nucleation centers in desired orientations and improve the quality of thin film as it grows thicker. Similarly, during oxidation of metal thin films, first atoms move due to increased substrate temperatures till it attains thermal equilibrium, during which the adatoms movements tries to achieve lower energy state. The proper plane orientation depends on the force of attraction and bond formation between metal and oxygen atoms.

Surface roughness

The root mean square surface roughness (at room temperature) of crystalline alumina substrate is 24.65nm . Table 1 shows that, surface roughness of tin oxide thin film deposited on alumina substrate. Higher substrate roughness of alumina, reduces the number of nanoparticles aligning in a given x-y plane. Deposition of thin film on rough surface provides point defects due to the formation of voids trapped between rough substrate surface and deposited thin film. However, low substrate roughness helps to form most of the nanoparticles in a given x-y plane [17] with less point defects.

Table 1. Root mean square surface roughness(rms) of tin oxide thin film for different temperatures

Oxidation Temperature(^{0}C)	Root mean square surface roughness (nm)
160	26.93
200	25.15
250	23.47
300	23.10

From the table it is seen that, the rms surface roughness of tin oxide thin film on alumina decreases with increase in oxidation temperature. The variation of surface roughness during oxidation depends on grain growth and reduction in point defects of the thin film. As the oxidation temperature increases, the surface roughness is expected to increase, due to crystallization and grain growth with drastic grain agglomeration [18-20]. If more point defects are available, the oxygen atoms can work together to design the substrate-film interface that suits the adatoms best with substrate. The films obtained in this work show grain growth due to increase in oxidation temperature (fig. 2), the decrease in rms surface roughness may be due to more point defects in the film.

Contact Angle

Contact angle (CA) of tin oxide thin film oxidized at different temperature is as shown in figure 3.

The contact angle of tin oxide deposited on alumina decreases with increase in oxidation temperature. The contact angle of tin oxide thin film being higher (155^0) for lower oxidation temperature might be due to the lower surface roughness obtained of the tin oxide thin films. The surface roughness obtained by surface profiler though not very reliable gives a rough idea about the nature of the surface. These films show hydrophobic nature. As oxidation temperature increases, the film shows hydrophilic nature with low contact angle (70^0). The surface roughness of the tin oxide thin films on alumina decreases due to increase in oxidation temperature due to which the contact angle also decreases with oxidation temperature.

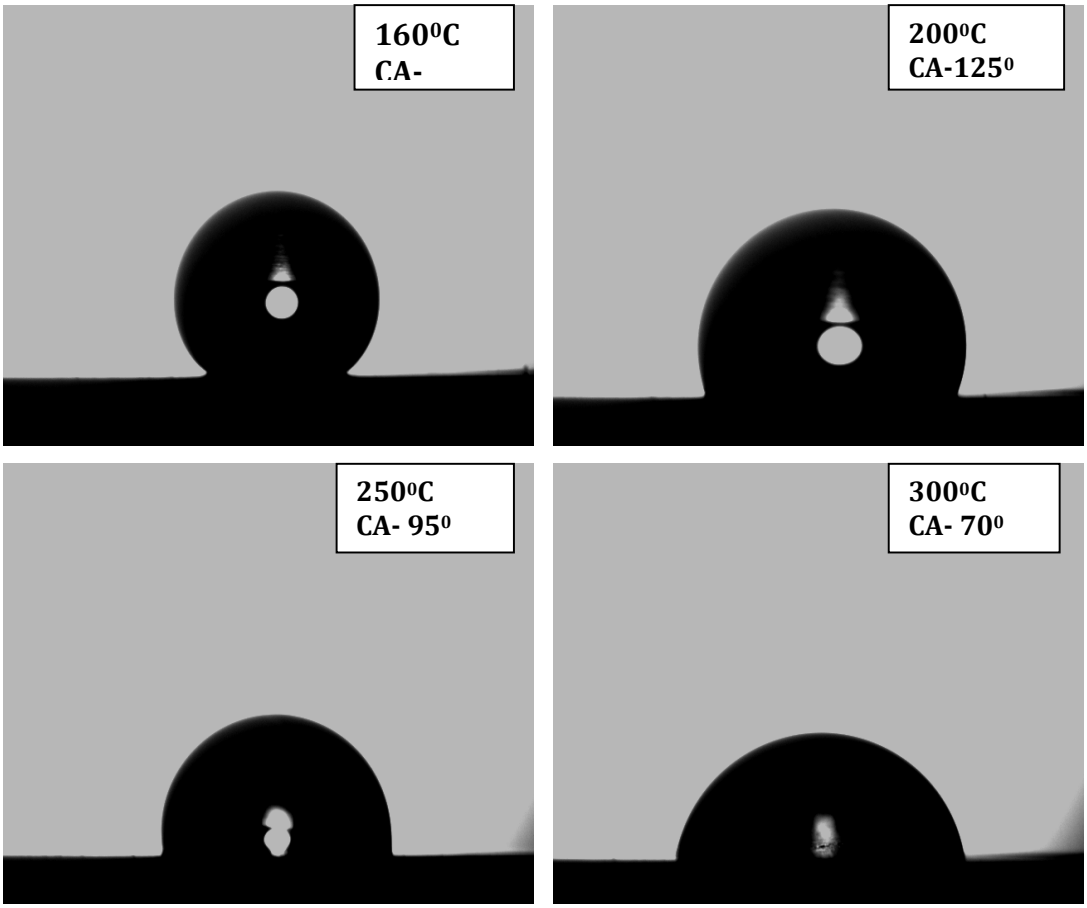

Fig. 3. Contact angle of tin oxide thin film oxidized at different temperatures

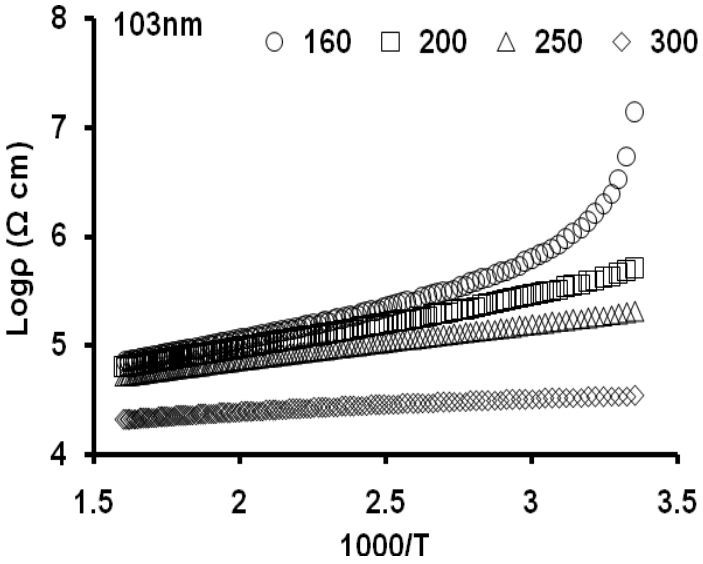

Fig.4.Variation DC electrical resistivity of tin oxide thin film on alumina substrate

DC Resistivity

Figure. 4 shows the graph of logρ vs 1000/T which reveals that the resistivity of the sample decreases with increase in a temperature showing the semiconducting behavior of the samples.

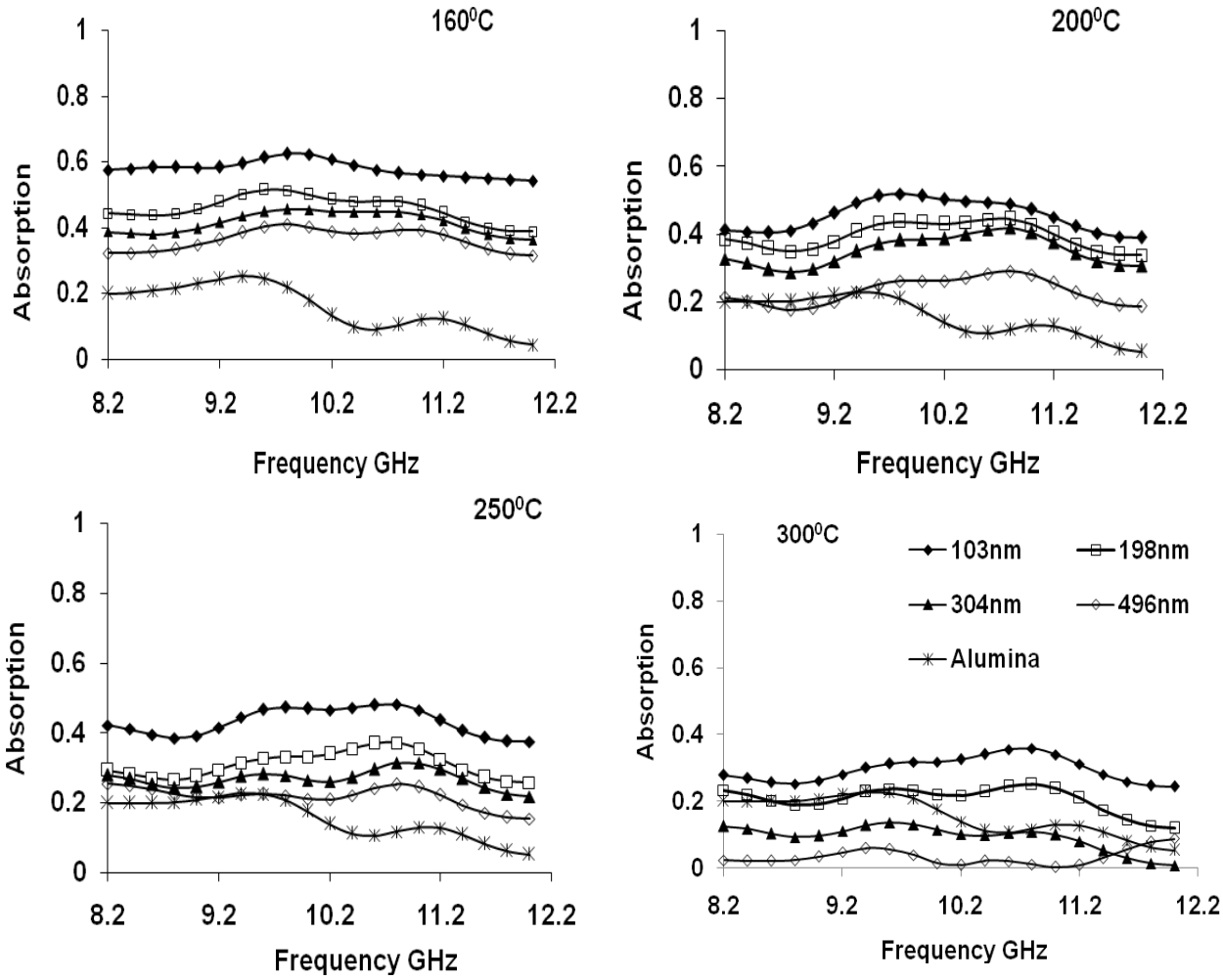

Fig. 5. Microwave absorption of tin oxide thin films as a function of frequency

At the room temperature, electrical resistivity of tin oxide thin film is of the order of 10^7 Ωcm. As oxidation temperature increased, the resistivity of tin oxide thin film decreased. The results obtained from the DC resistivity measurements are in good agreement with the surface morphology. It was found that; resistivity was high due to small grain size, high porosity and less defect inside the crystallites.

In general, the electrical properties of thin films usually differ from those of bulk material because of the essential differences in the microstructures and the geometrical limitations. Resistivity is actually the result of the combined factors such as grain size, crystal structure, defects and microstructure homogeneity. The high room temperature resistivity obtained in this work can be attributed to smaller grain size of the samples. Smaller grains imply large number of insulating grain boundaries and hence greater energy barrier to electron conduction resulting thereby in higher resistivity.

The activation energy represents the location of trap levels below the conduction band. The activation energy of tin oxide thin film changes with change in oxidation temperature. As oxidation temperature of film increased the activation energy increased. The grain boundaries scattering is predominant there is less activation energy and at

higher temperature the activation energy was high which indicates the position of trap levels in the semiconductor forbidden band towards the lower limit of the conduction band. The activation energy of tin oxide thin film was 0.023eV for low oxidation temperature whereas for higher oxidation temperature it was 2.37eV.

Microwave absorption

Figure 5 shows the microwave absorption in the X-band due to different oxidation temperatures. Thickness and oxidation temperature dependent microwave absorption was observed. The tin oxide thin film of lower thickness and lower oxidation temperature showed ~ 0.6 absorptance as compared to ~ 0.2 for bare alumina.

Absorption of tin oxide thin films decreased as thickness increased. As oxidation temperature was increased, the film of smallest thickness (103 nm) showed high absorption whereas the film of highest thickness (496 nm) showed very low absorption. In case of tin oxide, for higher oxidation temperature the low dielectric loss was obtained resulting low absorption and the surface morphological studies reveals that the nanosized grains were formed for tin oxide resulting in high surface area and hence, high absorption (~0.6) over the whole 8-12 GHz frequencies at lower oxidation temperatures and as oxidation temperature increased the grain size also increased and results in low absorption of tin oxide. An interesting result obtained was that due to increase in oxidation temperature the absorption of thicker films becomes lesser than that of alumina.

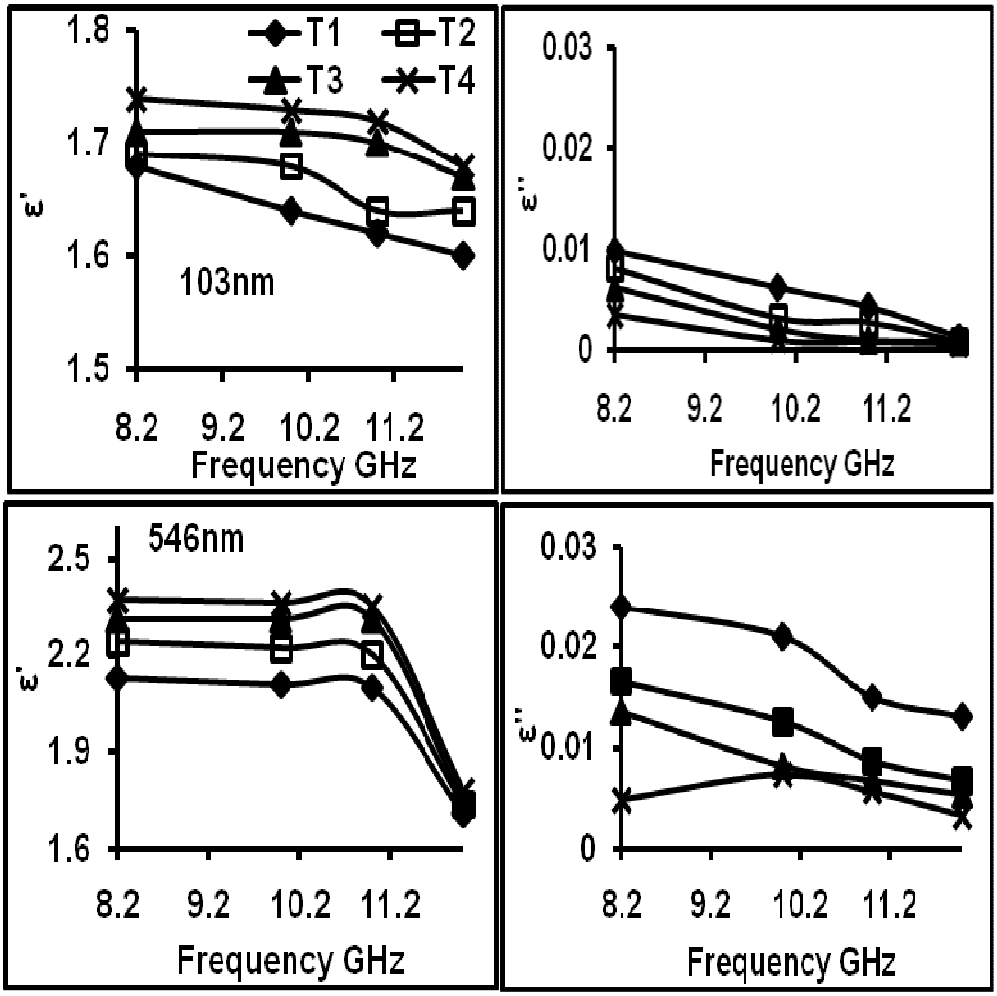

Fig 6. Permittivity of tin oxide thin film as a function of frequency on alumina [T1=160^{0}C,T2=200^{0}C, T3=250^{0}C and T4=300^{0}C]

Microwave Permittivity

Figure 6 shows the graph of real (ε') and imaginary part (ε") of permittivity versus thickness for different frequencies. Using the distance between maxima in the VSWR slotted section method, the real and imaginary part of dielectric constant was calculated using the Clapham equation [12]

$$\varepsilon' = \left(1 + \frac{\Delta\phi \times \lambda_0}{360 \times d}\right)^2 \qquad \varepsilon'' = \left(\frac{\Delta A \lambda_0 \sqrt{\varepsilon'}}{8.686 \pi d}\right)$$

Where, $\Delta\phi$ =Phase angle in degree, λ_0= Guided wavelength, d = Thickness of film

ΔA = Difference in attenuation in dB

The ε' of alumina is 10.2 for all frequencies and ε'' is 0.009. The ε' of tin oxide thin film at (8 to 12 GHz) microwave frequencies varies from 1.6 to 2.38. Low dielectric constant was observed for lesser oxidation temperature. From the figure it is seen that both ε' and ε'' decreases with increase in frequency. Generally oxides are reported to exhibit high polarisability and high dielectric constant, which extend in to microwave range. The frequency dependent dielectric permittivity is dominated by reorientation of molecular dipoles. At higher frequencies the orientational polarization vanishes and polarisability is determined by the localized electronic states, the relative permittivity decreases. This dielectric behavior of the sample can be explained by mechanism of polarization [21] and also the losses may mainly be caused by grain size and porosity. Interfacial polarization plays an important role in porous materials. As temperature increases, agglomeration increases and hence density increases. Therefore dielectric constant increases with oxidation temperature. Imaginary part of dielectric constant (ε") varies between 0.0064 and 0.024. Imaginary part indicates the extent of dielectric loss in the film. As temperature of oxidation increases the dielectric loss decreases.

CONCLUSION

Tin oxide thin films deposited by thermal oxidation (in air) of vacuum evaporated tin films on alumina are polycrystalline in nature with normal tetragonal rutile structure. The grain size of the tin oxide thin film deposited on alumina substrate increases with increase in oxidation temperature. Due to increase in oxidation temperature the tin oxide thin films change from hydrophobic to hydrophilic. These tin oxide thin films have less absorbing nature and it was observed that absorption decreases with increase in oxidation temperature. As oxidation temperature increased, dielectric constant also increased whereas dielectric loss decreased. For particular thickness and oxidation temperature, the tin oxide thin films showed absorption lesser than alumina. Such type of materials can have applications as overcoat on microstrip components to improve the properties.

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