Dielectric and Optical Properties of Zirconium Titanate Thin Films by Reactive DC Magnetron Co-Sputtering

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ABSTRACT

Zirconium titanate thin films were deposited on alumina substrates by DC magnetron reactive co-sputtering by varying substrate temperature and the effects of substrate temperature on optical and dielectric properties of the films have been studied intensively by available characterization techniques. The optical parameters were determined by Swanepoel's method. The films exhibited high transmittance in the visible region and the optical band gap of the films varied from 3.1 to 2.8 eV as the temperature varied from 33 to 400°C. The film deposited at room temperature exhibit a high transmittance of 71%. Dielectric constant measurements have been carried out at 10 GHz of frequency. The dielectric constant increased with increase in temperature and the film deposited at 400°C exhibited a high dielectric constant (40) and a low dielectric loss (0.026).

Index Terms — **zirconium titanate thin films, DC magnetron reactive co-sputtering, 19 alumina substrate and substrate temperature**

1 INTRODUCTION

HIGH-K dielectric materials find applications in dielectric resonators, filters, gate dielectrics, phase shifters, voltage tunable oscillators and dynamic random access memories [1]. Owing to their high dielectric constant, high quality factor, high temperature stability besides good optical properties Zirconium titanate (ZTO) and ZTO based materials act as potential candidates for microwave dielectrics [2-4] and also find applications in mid-infrared integrated photonics as well [5]. There are reports on the effects of processing parameters like substrate temperature [6], annealing temperature [7, 8] and partial pressure ratios of sputtering and reactive gases [4] on the dielectric properties of ZTO films. Some of the authors described correlation of processing parameters and film properties. Kim *et al* reported the effects of thickness on dielectric behavior of ZTO thin films fabricated by sol-gel process [9]. Kim *et al* demonstrated effects of microstructures on microwave dielectric properties of ZTO thin films [10]. Victor *et al* reported the significance of amorphous ZTO thin films and the dielectric relaxation phenomenon in these films [11]. Kim *et al* correlated strain and dielectric properties of ZTO thin films [1]. Kim *et al* described effects of substrate temperature on physical and dielectric properties of ZTO thin films in the MHz to GHz range by measuring dielectric constant in the range of 2 to 6 GHz [6, 10].

During nucleation, the smaller crystallites move randomly on the surface of the substrate and combined with adjacent crystallites to grow in to larger crystallites resulting crystallanity of the film, hence all the films remained in amorphous state because of the surface roughness of the substrate where as ZTO films deposited on glass substrate

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(smooth surface) exhibited crystallanity [8]. The reason is that the rough surface restricts the motion of crystallites. However, both crystalline and amorphous ZTO films find the applications in microwave communication, MMIC and VLSI.

Some reports described the dielectric properties of ZTO films on different substrates [12-14]. Pamu *et al* deposited ZTO on to platinized Si substrates by direct current (DC) magnetron sputtering [4]. Kim *et al* reported dielectric properties of ZTO films deposited on phosphorous-doped Si (100) substrate by RF sputtering and the mentioned affects of substrate texture on microstructures and strain of the films, which in turn affected the dielectric property of the films as they are correlated [1]. The surface modification, particularly coatings deposition is beneficial to tissue-engineering applications [15]. Salahinejad *et al* discussed nano structured inorganic ZTO films deposited on medical grade stainless steel substrates by sol-gel process and correlated the biocompatibility of the films with their surface structure [16]. There are reports on ZTO films deposited on microscopic glass plates [8, 17]. Victor *et al* investigated relaxation and conduction mechanisms of ZTO films deposited on Pt coated Si substrate by a KrF (248 nm) pulsed excimer laser ablation [18].

The surface texture of the substrate shows a high impact on the films. However there are very few reports on dielectric properties of DC magnetron reactive co sputtered ZTO films on alumina substrates. Hence in the present study ZTO thin films have been deposited on alumina (Al_2O_3) substrates by varying substrate temperature to study the dielectric behavior as a function of temperature at a steady frequency of 10 GHz.

2 EXPERIMENTAL DETAILS

ZTO thin films were deposited by employing VR SPU-04D DC magnetron sputtering unit equipped with rotary and diffusion pumps, pirani and penning gauges, GFC17 Aalbarg mass flow controllers, zirconium and titanium targets (99.99% pure) and ultra pure (99.99%) argon and oxygen gases. Alumina substrates with dimensions of 75 mm × 25 mm × 0.5 mm were used in the present study.

Initially the substrates, deposition chamber and substrate holder were thoroughly cleaned before carrying out each deposition. The chamber was evacuated to a base pressure of $9X10^{-6}$ mbar to increase the mean free path of the sputtered atoms and to avoid the contamination of the films. Here the substrates were placed on a holder, which also acts as a substrate heater. This facilitates the uniform distribution of heat through the substrates. Target to substrate holder distance was fixed as 60 mm. Then the sputtering gas, argon was injected in to the chamber and the chamber pressure was allowed to settle down to a working pressure of $4\text{-}5 \times 10^{-4}$ mbar then the targets were pre sputtered to remove any oxide layer on the target surface. Sputtering powers of Zr and Ti targets were maintained as 130 to 180 and 80 to 180 watt respectively. Argon (30 sccm) and oxygen (2 sccm) gases allowed through individual mass flow controllers get mixed up in their path while entering the chamber. Then the targets were sputtered in argon and oxygen atmosphere. The sputtered target atoms react with oxygen atoms in the vicinity of the target or on their path or on the substrate surface to form respective oxides. During the deposition process, the substrates were heated to enhance the structural and mechanical properties of the films.

Structural characterization of the films has been carried out by Rigaku smart lab (9 kW) diffractometer operated at 30 kV and 10 mA in the range of 20-80^o with Cu-k$_\alpha$(λ= 1.5418 A^o) radiation at a scanning rate of 0.02^o/min. Surface morphological images of the films have been obtained by employing NT-MDT NTEGRA-PRIMA atomic force microscope (AFM). The optical parameters of the films have been studied by recording transmission spectra of the films by Hitachi U-3400 UV/VIS spectrophotometer. Agilent Technologies network analyzer at a frequency of 10 GHz has measured dielectric constant and loss of the films.

3 RESULTS AND DISCUSSION

3.1 STRUCTURAL PROPERTIES

The X-ray diffraction (XRD) patterns of the films are shown in the Figure 1. All the films exhibited amorphous characteristics even at 400^{o}C of temperature. This may be due to the fact that some of the material thin films require very high temperatures to get crystallized [8]. Evolution of crystallinity in ZTO films, deposited on microscopic glass slides started at 150^{o}C and showed an intense peak at 250^{o}C. Later on crystallinity got diminished at 300^{o}C [19] but here ZTO films on alumina remained in amorphous state even at 400^{o}C. This can be attributed to insufficient energy to crystallize films on alumina substrates while films deposited on glass crystallized at 200^{o}C [1]. The films on alumina may crystallize at higher temperatures. This clearly evidences the dependence of degree of crystallinity in ZTO films on the substrate material. On the other hand, very high temperatures destroy the microstructure of the films and zirconium evaporates

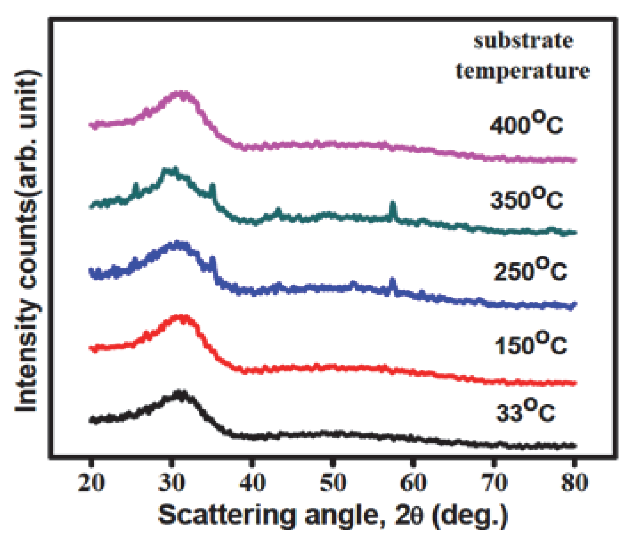

Figure 1. X-ray diffraction patterns of ZTO thin films deposited on Alumina substrate at different temperatures.

and vanishes at higher temperatures [20]. However, amorphous ZTO films are desirable candidates for monolithic microwave integrated circuits (MMIC) and ultra large scale integration (ULSI) devices [11]. Though the films are amorphous, AFM images revealed the re arrangement of the grains at higher temperatures.

3.2 SURFACE MORPHOLOGICAL PROPERTIES

The digital 3D AFM images of ZTO thin films on alumina substrates as a function of substrate temperature are illustrated in the Figures 2(a) - (e). From the images, it is observed that there is an increase in the roughness of the surface of the films and the variation is shown in Figure 2f. This can be attributed to the random mobility of the deposited atoms at higher temperatures. At high temperatures, individual grains combine to grow in size, which reduces the spacing among them. Consequently, films became crack free and exhibited columnar structure. It is also evidenced that the films became dense at higher temperatures due to thermal treatment particularly the film deposited at 400°C exhibited highly densely packed structure.

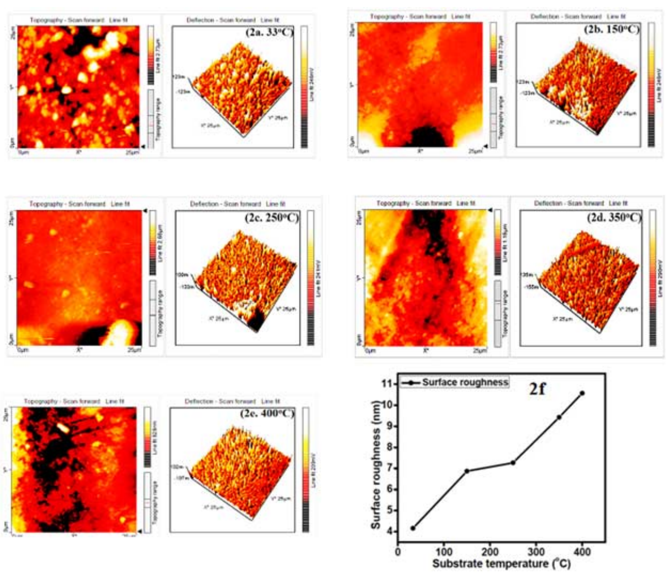

Figure 2. AFM images of ZTO films deposited at (a) 33 °C, (b) 150 °C, (c) 250 °C, (d) 350 °C, (e) 400 °C and (f) shows the variation of surface roughness of the films.

3.3 OPTICAL PROPERTIES

Transmittance spectra of ZTO thin films have been recorded within a wavelength range of 200 to 900 nm. From the spectra shown in Figure 3, it is observed that all the films are highly transparent in the visible region but the transmittance decreased with increase in temperature due to the increased density in the films and due to availability of more energy states for photons to get absorbed and also increase in density and surface roughness results in increased number of collisions among the incident atoms which in turn leads to an increase in absorbance and hence a decrease in transmittance. Transmittance of the films varied as 71, 67, 67, 65 and 63% with variation of temperature as 33, 150, 250, 350 and 400 °C respectively. The transmittance of ZTO films on

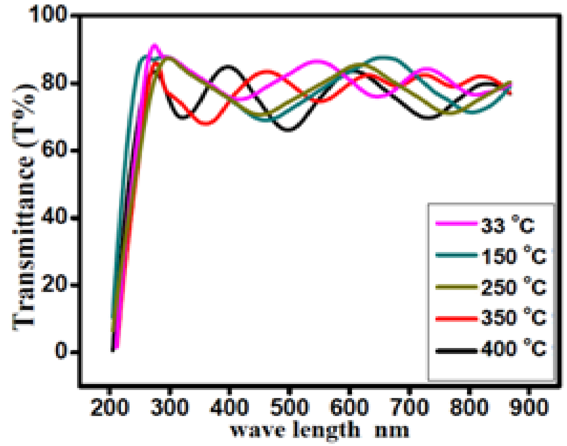

Figure 3. Transmittance spectra of ZTO films deposited at different temperatures.

alumina is found to be less compared to those films deposited on glass substrates [19]. The absorption co efficient can be obtained in the strong absorption region [21] by

$$\alpha=\frac{1}{t}*\ln\frac{(1-R^2)+((1-R^4)+4R^2T^2)^{1/2}}{2T}\ \text{eVm}^{-1} \qquad (1)$$

where, t is the thickness of the film on the substrate measured with step-mask method usi ng stylus surface profilometer (245 nm), T is the transmittance and R is the reflectance of the material film. The absorption co efficient, α is related to the photon energy, hν [22] as

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

where, A is a band edge constant, ν is the photon transition frequency and n characterizes the nature of the band transition. i.e., n=1/2 and 3/2 correspond to direct allowed and direct forbidden transitions and n=2 and 3 correspond to indirect allowed and indirect forbidden transitions respectively. The optical band gap energy can be obtained by the extrapolation of linear portions of $(\alpha h\nu)^2$ vs. hν plot to hν=0. The band gap energy reduced from 3.1 to 2.8 eV with increase in temperature as shown in Figure 4. The optical bandgap depends

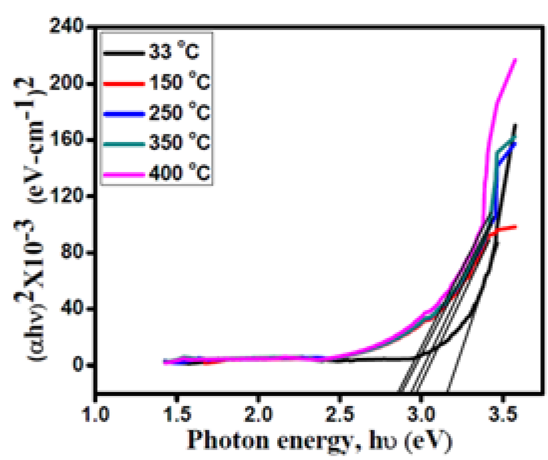

Figure 4. Tauc's plot of ZTO films deposited at different temperatures.

inversely on crystallinity. In the present study, though the films are amorphous the grains get absorbed by other grains and combine each other under applied substrate temperatures. Hence, the optical band gap decreased with increase in substrate temperature.

The refractive index of the film, n_1 in the transparent, weak and medium absorption regions can be calculated [21] by:

$$n_1 = (N_1 + (N_1^2 - S)^{1/2})^{1/2}. \quad (3)$$

where, $N_1 = \frac{2s}{T_M} + \frac{(s^2+1)}{2}$ for transparent region and $N_1 = 2s(\frac{T_M - T_m}{T_M T_m} + \frac{s^2+1}{2})$ for weak and medium absorption regions. Where, T_M and T_m are the transmittance maximum and minimum respectively at a certain wavelength. Here the refractive index varied from 2.1 to 1.9 with increase in temperature. The extinction coefficient can be given [21] by:

$$k = \frac{\alpha\lambda}{4\Pi} \quad (4)$$

The extinction coefficient showed a similar fashion of refractive index of the films and decreased from 1.9×10^{-3} to 1.3×10^{-3} and is shown in Figure 5 along with variation of refractive index of the films.

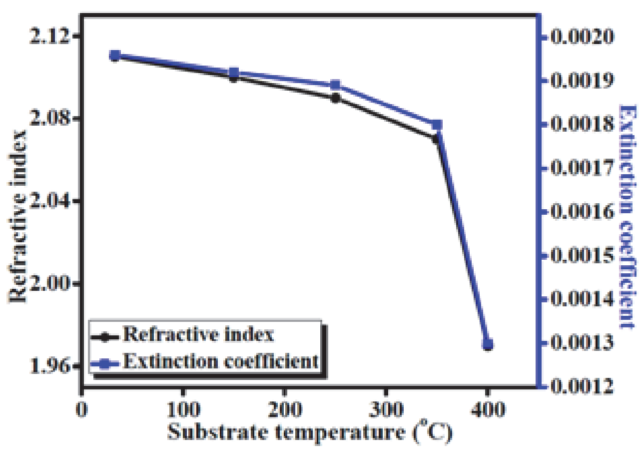

Figure 5. Refractive index and extinction coefficient of ZTO films as a function of substrate temperature.

The packing density of the deposited films can be obtained [21] from:

$$p = \frac{n_f^2 - 1}{n_f^2 + 2} * \frac{n_b^2 + 2}{n_b^2 - 1} \% \quad (5)$$

where n_b is the bulk refractive index and n_f is the refractive index of the thin films. The packing density of the films increased from 79 to 94% with temperature. The corresponding plot is shown in Figure 6.

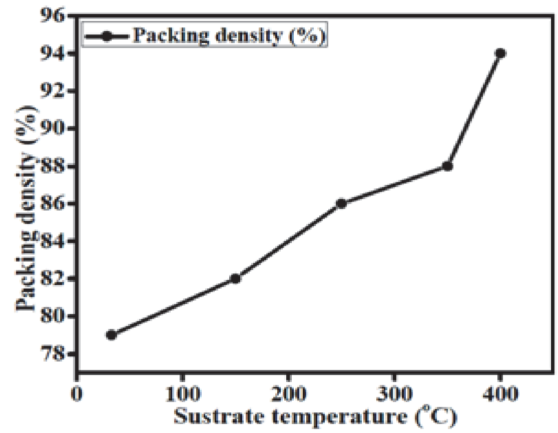

Figure 6. Packing density of ZTO films as a function of substrate temperature.

3.3 DIELECTRIC PROPERTIES

High frequency dielectric measurements were carried at 10 GHz and are shown in Figure 7 (a) - (b). The dielectric constant got enhanced from 19 to 40 with increase in substrate temperature from 33 to 400 °C. This enhancement can be attributed to the improved structural properties of the films due to rearrangement of the grains by increased surface mobility with increase in temperature. The dielectric loss (tan δ) of the films showed an overturn behavior to that of dielectric constant and was reduced from 0.074 to 0.026 with increase in temperature. The film deposited at 400°C exhibited superior dielectric constant and less dielectric loss. The high-k value makes the films to act as potential candidates for microwave applications and the low optical loss of ZTO thin films makes them suitable to integrated middle infrared (MIR) photonic device fabrication [5].

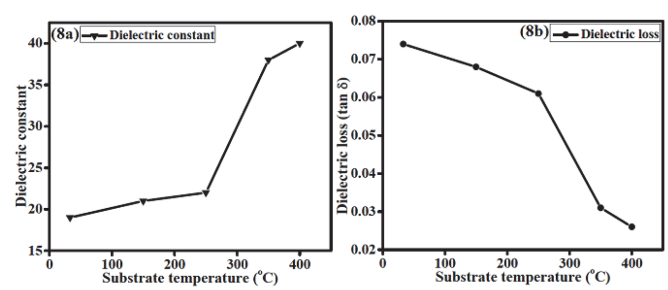

Figure 7. Variation of (a) dielectric constant and (b) loss of ZTO films with substrate temperature.

4 CONCLUSIONS

ZTO thin films were deposited by reactive DC magnetron co-sputtering on alumina substrates to study the optical and dielectric properties as a function of substrate temperature (33, 150, 250, 350 and 400°C) and the results were compared with ZTO films deposited on glass substrates. Although the films are amorphous in nature, they exhibited good optical and dielectric properties. AFM images evidenced crack free and densely packed structure of the films. The optical transmittance of the films is less than those films deposited on glass substrates and it decreased with increase in temperature while the dielectric constant increased with increase in substrate temperature. The films deposited at 400°C exhibited maximum dielectric constant (40), minimum dielectric loss (0.026), densely packed structure (94%) and minimum transmittance (63%). Hence, it concluded that the substrate temperature enhanced ZTO film properties.

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