

Optical and Dielectric Properties of Pulsed Laser Deposited Nanocrystalline ZnTiO₃ Thin Films

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Abstract: Zinc titanate (ZnTiO₃) target was prepared by conventional solid state reaction method using ZnO and TiO₂ in a molar ratio of 1:1. ZnTiO₃ thin film have been deposited on ITO coated glass substrate using pulsed laser deposition (PLD) technique employing a KrF laser source ($\lambda=248$ nm). In present work, the effect of substrate temperature on the structural, optical and dielectric properties of ZnTiO₃ thin film has been studied. The XRD pattern revealed that pure hexagonal phase of ZnTiO₃ appear upto 400 °C and more increment in substrate temperature leads to transformation of hexagonal phase to cubic phase. We have observed the blue shift in absorption edge at lower temperature. When the substrate temperature increases from 300 to 400 °C the band gap decreases due to strong hexagonal phase, but more increment in substrate temperature increases the band gap causes by change of phase from hexagonal to cubic. The dielectric constant of ZnTiO₃ thin film increases as the substrate temperature increases due to the enhancement in crystallinity. The improved film morphology by the increment in substrate temperature might also contribute to the enhancement of dielectric properties.

1. INTRODUCTION

ZnO and TiO₂ is wideband semiconductor with excellent properties and extensive applications, and have attracted much interest on either single material [1-4] or ZnO–TiO₂ composites [5-6]. Dulin and Rase [7] showed that three compounds exist in the ZnO–TiO₂ system, including Zn₂TiO₄ (cubic), ZnTiO₃ (hexagonal and cubic), and Zn₂Ti₃O₈ (cubic). Zn₂TiO₄ phase can easily be prepared by conventional solid-state reaction. While, the stable formation of ZnTiO₃ phase was known to be complicated, mainly due to the decomposition of ZnTiO₃ into Zn₂TiO₄ and rutile TiO₂ at about 945 °C.

ZnTiO₃ is an attractive material for applications in microwave dielectrics [8-11]. Because of its relatively low sintering temperature and good dielectric properties, ZnTiO₃ has been regarded as a good candidate for low-temperature cofired ceramics (LTCCs), by which some novel multilayer communication modules involving the integration of passive component can be applied. From an industrial perspective, ZnTiO₃ is an active catalyst, paint pigment and phosphor, owing to its good semiconducting and dielectric properties. ZnTiO₃ is also a good regenerable sorbent for desulphurization of hot coal gases. Enhanced catalytic and luminescent properties have also been demonstrated by using nanocrystalline ZnTiO₃ [12-14].

ZnTiO₃ belongs to the limonite structure which is a derivative structure of corundum, Zn⁺² and Ti⁺⁴ occupy 2/3 octahedral voids leaving the rest of the 1/3 octahedral voids empty and the columbic repulsion between Zn⁺² and Ti⁺⁴ ions causes each to move slightly towards the adjacent unoccupied octahedral site. The oxygen ions also shift slightly from idealized hexagonal closed packed positions [15].

Several reports are evident in the literature on the characteristics of ZnTiO₃ powder prepared by solid state reaction and sol–gel methods [16-17]. Kim et al. and other researchers [18-20] also tried to obtain the suitable dielectric properties by controlling composition in ZnO–TiO₂ binary system and/or substituting zinc with barium, calcium, strontium and magnesium. Most of those studies involve only bulk system. References concerning the characteristics of zinc titanate based thin film are lacking.

2. EXPERIMENTAL DETAILS

(i) Film preparation:

The ZnTiO₃ target was prepared by conventional solid state reaction using 99.99% pure ZnO and TiO₂ powder in a molar ratio 1:1 as the starting materials (Loba Chemie, India). The starting materials were ground for 24 h and then calcined at 400 °C for 12 h. The calcined powder was reground for 6 h and was then pressed into pellets of 1.5 cm in diameter and 1.15 mm thickness under the pressure of 90 MPa. Then, the pellets were sintered at temperatures of 800 °C for 12 h. A KrF excimer pulsed laser system (wavelength $\lambda = 248$ nm) was used for the deposition of thin films. The pulse repetition rate was 10 Hz with laser fluence of about 2–3 J cm⁻². The target to substrate distance and working O₂ pressure were kept 35 mm and 50 mTorr respectively. The thickness of the grown film is typically ~200 nm.

(ii) Film characterization:

The phase and orientation of as-grown thin films were characterized by X-ray diffractometry (XRD, Bruker AXS D-8 Advance Diffractometer) using CuK α ($\lambda=1.5407$ Å) radiation. The surface topography and microstructure were examined by atomic force microscope (NTMDT: NTEGRA model). Absorption spectra have been taken using UV-vis-NIR spectrophotometer (Varian Cary 5000) in the wavelength range

200 to 800 nm. Dielectric properties of thin films grown on ITO glass substrate were studied using impedance analyzer.

2. RESULTS AND DISCUSSION

3.1 Structural properties

It is generally difficult to synthesize single phase ZnTiO₃ due to the presence of both cubic and hexagonal phases at low temperature and the decomposition into Zn₂TiO₄ and TiO₂ (rutile) at high temperature, therefore, several parameters need to be optimized. In our previous work we have optimized the condition for synthesize the pure single hexagonal phase of ZnTiO₃ ceramics [21]. In present work we have studied the effect of substrate temperature on growth of ZnTiO₃ thin film on to ITO coated glass substrate using pulsed laser deposition technique. Figure 1 shows the XRD patterns of the thin films at different substrate temperatures varying from room temperature to 550 °C. At room temperature film was amorphous nature, only single peak appear of substrate. When we increase the substrate temperature from room temperature to 300 °C hexagonal phases starts to appear and become more intense at 400°C. Further increases in substrate temperature the XRD pattern shows the coexistence of both cubic and hexagonal-phases.

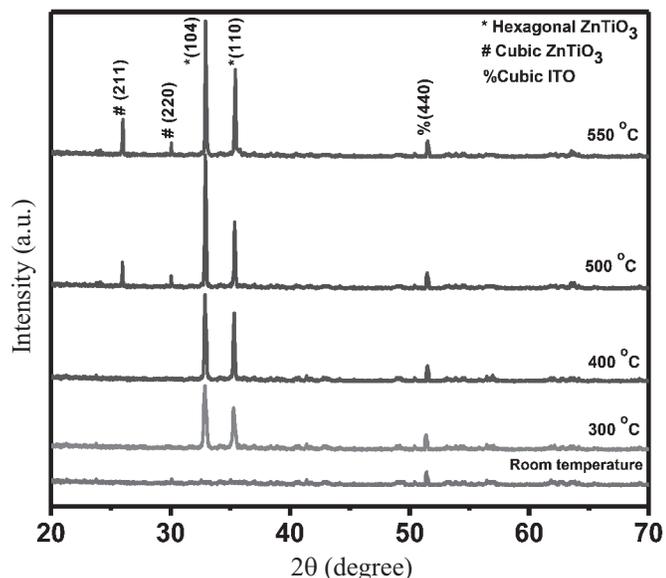


Fig 1: XRD patterns of ZnTiO₃ thin film at different substrate temperatures

The crystallite size of these samples were calculated along the (104) orientation of hexagonal ZnTiO₃ phase using the Scherrer's formula. The crystallite size of the thin films at various substrate temperature calculated using Scherrer's formula are shown in Table 1 and the variation of FWHM and crystallite size are shown in Figure 2. It is found that the crystallite size increases and FWHM decreases with increasing the substrate temperature. According to Ostwald ripening [22], the increase in the particle size is due to the merging of the smaller particles into larger ones and is a result of potential energy difference between small and large particles and can

occur through solid state diffusion. The percentage of hexagonal-phase was estimated approximately from the ratio of areas of hexagonal-phase peaks to the areas of all peaks using the equation as follows:

$$H (\%) = \frac{A_h}{A_{all}} \times 100 \quad (1)$$

Here, A_h and A_{all} denote the areas of hexagonal-phase ZnTiO₃ and the areas of all peaks, respectively. The results are summarized in Table 5.1

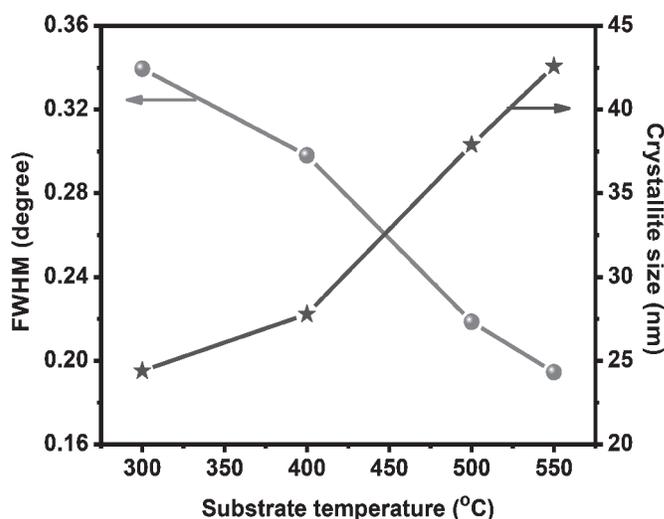


Fig 2: Variation of FWHM and crystallite size with substrate temperature

Table 1: Various parameters of ZnTiO₃ thin films deposited at different substrate temperature.

Substrate temperature (°C)	Lattice Constants		Unit cell volume (Å ³)	Hexagonal phase percentage (%)	FWHM (degree)	Crystallite Size (nm)	Grain size AFM (nm)
	a (Å)	c (Å)					
300	5.086	13.86	310.4	100	0.3395	24.39	43
400	5.078	13.85	309.38	100	0.2981	27.78	61
500	5.074	13.85	308.73	64.65	2.7191	37.9	85
550	5.066	13.85	307.74	59.33	0.1945	42.58	102

Figure 3 shows the variation of lattice parameter and unit cell volume with substrate temperature. It is found that lattice parameter and unit cell volume decreases with substrate temperature. This is because of shifting the (104) peak to larger angle indicating the existence of residual stress due to different thermal expansion coefficients between ZnTiO₃ film and substrate after cooling down [23]. Compared to the unstressed bulk value of a=5.077 Å, the large value of lattice constant for ZnTiO₃ film grown at room temperature shows that the unit cell is elongated along the a axis, and compressive force acts in the plane of the film. As substrate temperature increases, the compressive force decreases, however, as the substrate temperature reaches to 400°C, the lattice constant of the ZnTiO₃(104) films becomes shorter than that of bulk ZnTiO₃, which indicates that the compressive stress in the film plane changes to a tensile one with substrate temperature increasing.

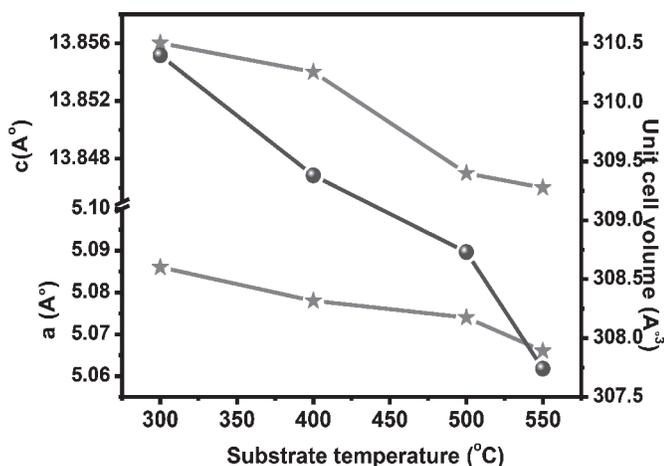


Fig 3: Variation of lattice parameter and unit cell volume with substrate temperature

Figure 4 shows the AFM image of the ZnTiO₃ thin film deposited at different substrate temperature. The RMS roughness and the average columnar grain size were calculated from the AFM images and their variation with substrate temperature is shown in Figure 5. The average grain size increased from 43 nm to 102 nm and surface roughness increases from 5 nm to 10 nm over the substrate temperature range. It is believed that high temperature provided enough energy for the atoms to get high surface mobility, which promote the formation of the larger columnar structure grains. The general increase in the surface roughness is due to the increase in the average grain size.

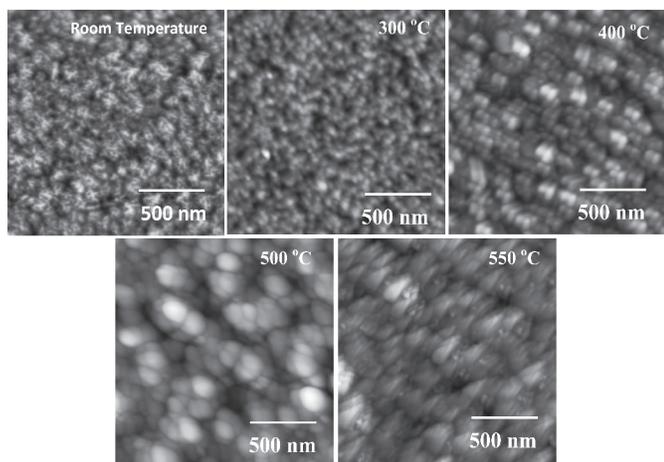


Fig 4: AFM image for a ZnTiO₃ thin film deposited at various substrate temperatures

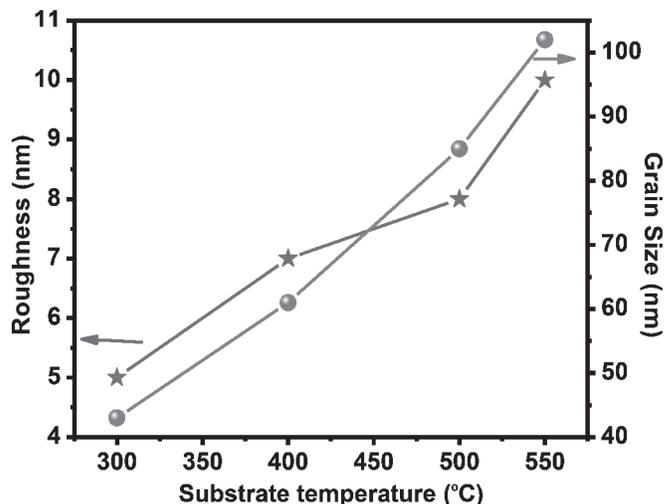


Fig 5: Variation of grain size and roughness with substrate temperature.

The optical absorption spectra of ZnTiO₃ thin film deposited at different substrate temperature are shown in Figure 6. One can see that the absorption edge of the crystalline thin film moves to longer wavelength as compared with that of amorphous film. It is also observed that the ultraviolet absorption edge of single hexagonal-phase ZnTiO₃ has a red-shift, compared with that of cubic/hexagonal mixed phase ZnTiO₃.

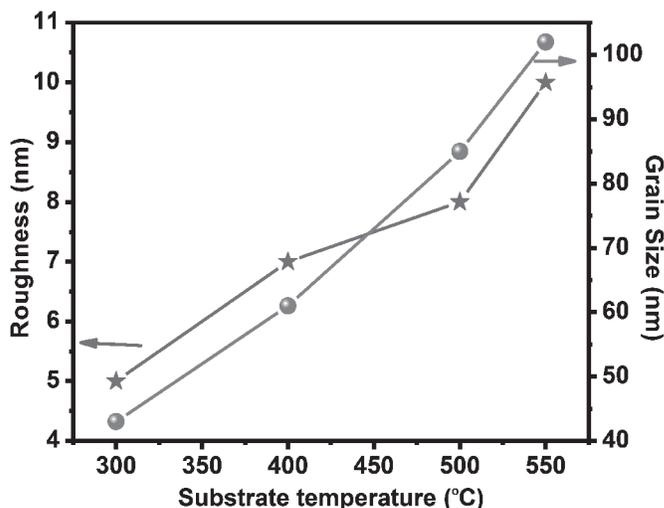


Fig 6: Optical absorption spectra of ZnTiO₃ thin film deposited at different substrate temperature

For the indirect band-gap semiconductor, the relation between the absorption edge and photon energy ($h\nu$) can be written as follows [24]:

$$\alpha h\nu = A (h\nu - E_g)^2 \tag{2}$$

where α is the absorption coefficient, A is a constant, h is Planck's constant, ν is the photon frequency and E_g is the optical band gap. The plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ of thin films deposited at different substrate temperature is shown in Figure 7. An extrapolation of the linear region of a plot of $(\alpha h\nu)^{1/2}$ on the y-axis versus photon energy ($h\nu$) on the x-axis gives the value of the optical band gap E_g . The best fitting of $(\alpha h\nu)^{1/2}$ versus ($h\nu$) was obtained for crystalline films, indicating that ZnTiO₃ is an indirect band gap semiconductor, which is consistent with the reported in literature [15]. The variation of band gap with substrate temperature is shown in inset of Figure 7. We have observed the blue shift in absorption edge is due to the poor crystallinity of ZnTiO₃ thin films grown at low temperature. The crystallinity of the ZnTiO₃ thin films grown below 400 °C was poor and exhibits polycrystalline structure. The physical model of the structure can be viewed as various nanocrystalline islands embedded in a matrix of amorphous ZnTiO₃. Qualitatively, the interatomic spacing of amorphous structure would be relatively long and more disordered than crystalline structure due to the absence of long-range translational periodicity. As the fraction of amorphous ZnTiO₃ phase increases in the films grown at low temperature, the extended localization in the conduction and valence bands increases [25]. As a result, the absorption of photon is mainly contributed by amorphous ZnTiO₃ and hence the absorption edge blue shifted. When the substrate temperature increases from 300 °C to 400 °C the band gap decreases due to strong hexagonal phase, but more increment in substrate temperature increases the band gap causes by change of phase from hexagonal to cubic.

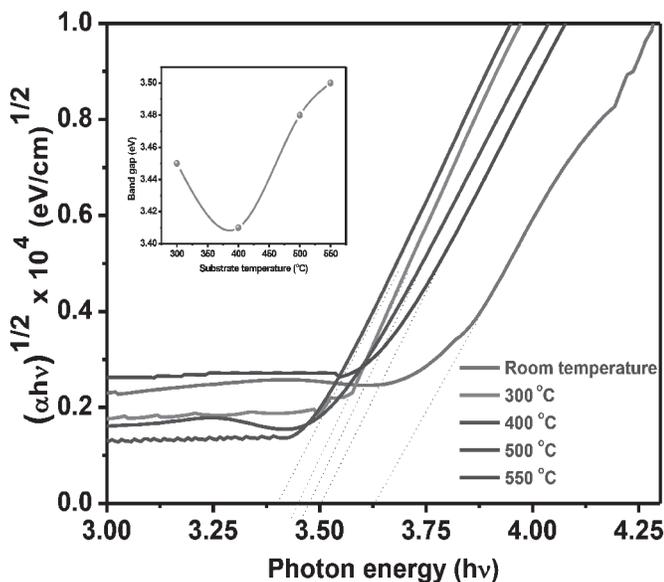


Fig 7: $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot of ZTO sintered at different substrate temperature. Inset shows the variation of band gap with substrate temperature.

Figure 8 and Figure 9 shows the relative dielectric constant and

loss tangent as a function of frequency in the range 500 Hz to 5 MHz of the ZnTiO₃ thin films deposited at different substrate temperature. Based on this, it is seen that the dielectric constant is steeply decreasing in the lower frequency region and has an almost constant value at the higher frequency region. The dielectric loss tangent followed the similar trend. This shows that there is not much frequency dispersion in the dielectric properties for ZnTiO₃ thin film, which is an important property suitable for many applications.

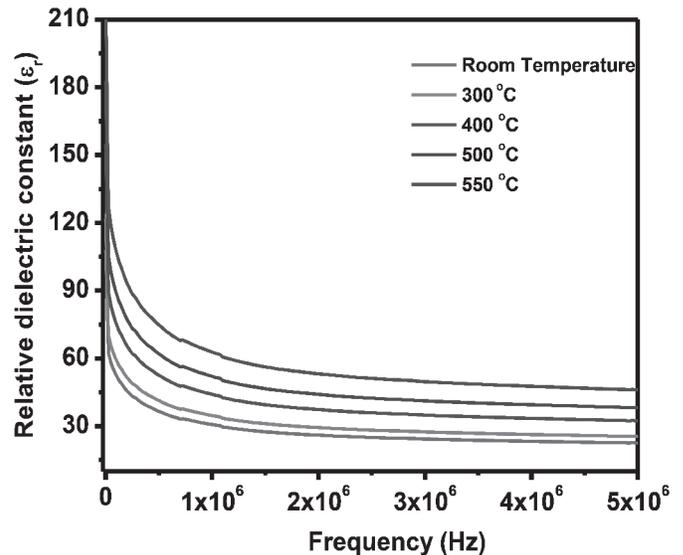


Fig 8: The relative dielectric constant as a function of frequency ZnTiO₃ thin films deposited at different substrate temperatures

Figure 10 shows the variation of relative dielectric constant and loss tangent with substrate temperature. The dielectric constant of ZnTiO₃ thin film deposited at room temperature is lowest due to its amorphous nature. When the substrate temperature increases, dielectric constant increases due to the enhancement in crystallinity. The improved film morphology by the increment in substrate temperature might also contribute to the enhancement of dielectric properties.

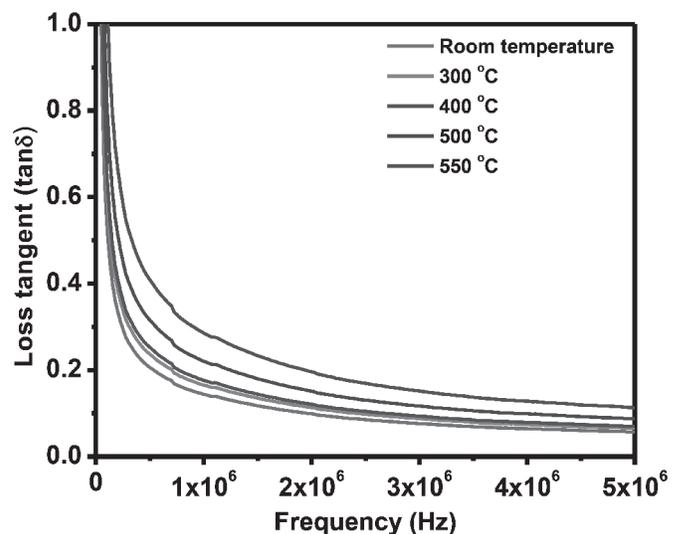


Fig 9: The loss tangent as a function of frequency ZnTiO₃ thin films deposited at different substrate temperatures

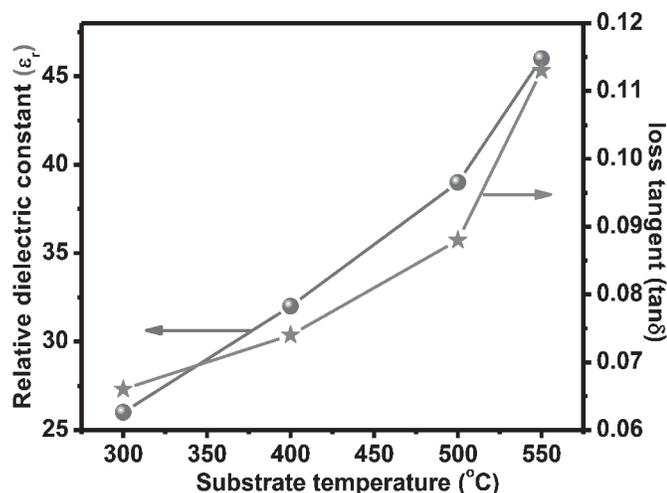


Fig 10: Variation of relative dielectric constant and loss tangent with substrate temperature

4. CONCLUSION

ZnTiO₃ thin film have been deposited on ITO coated glass substrate using pulsed laser deposition (PLD) technique employing a KrF laser source ($\lambda=248$ nm). At room temperature film was amorphous nature, only single peak appear of substrate. When we increase the substrate temperature from room temperature to 300 °C hexagonal phases starts to appear and become more intense at 400°C. Further increases in substrate temperature the XRD pattern shows the coexistence of both cubic and hexagonal-phases. It is also observed that the ultraviolet absorption edge of single hexagonal-phase ZnTiO₃ has a red-shift, compared with that of cubic/hexagonal mixed phase ZnTiO₃. We have observed the blue shift in absorption edge is due to the poor crystallinity of ZnTiO₃ thin films grown at low temperature. The dielectric constant of ZnTiO₃ thin film deposited at room temperature is lowest due to its amorphous nature. When the substrate temperature increases, dielectric constant increases due to the enhancement in crystallinity.



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