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Optical properties of pseudo binary oxides $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films prepared by spray pyrolysis techniqueChandrashekara H.D.^{a,b}, Basavaraj Angadi^{a*}, Shashidhar R.^a, Murthy L.C.S.^a, Poornima P.^c^a Department of Physics, Jnanabharathi, Bangalore University, Bangalore-560056, India.^b GSC, Department of Physics, Hassan-573217, India.^c GFGC, Department of Physics, H.N.Pura, Hassan-573217, India.

Abstract

Pseudo binary oxide thin films, $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$, were prepared by spray pyrolysis technique on cleaned quartz and silicon substrates. The prepared precursor solutions of Al_2O_3 and TiO_2 were mixed thoroughly in appropriate volume, calculated from the molar fraction. The XRD pattern of Al_2O_3 - TiO_2 film shows anatase phase and mixed phase of Al_2TiO_5 (Aluminum Titanium oxide). The SEM micrograph shows spherical grains with nano porous surface and some clusters, it is also composed of crumb like nano particles and average grain sizes are estimated. In the EDAX spectrum, the signals corresponding to oxygen (O_2), titanium (Ti), aluminum (Al) and substrate silicon (Si) are seen, elemental analysis shows that weight percentage are in stoichiometric ratio. Transmittance and Reflectance spectra were recorded in normal incidence by UV-Visible Spectrophotometer in wavelength range 350nm to 1200nm. Using these optical data the thickness, refractive index, extinction coefficient, real and imaginary part of dielectric constants, energy band gap, Urbach energy and Packing density are estimated. It is observed that, with the increase in molar fraction there is a variation of the energy band gap, which may be attributed to the mixed phase formation in the films as well as formation of defects. The obtained pseudo binary oxide thin films have wide band gap and porous surface structure; hence these films are further used for sensing application.

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1. Introduction

Studies on pseudo binary oxide thin films have increased in recent years due to their interesting properties such as lower leakage current [1]. Various binary oxides, such as CdO-ZnO, CuO-CeO₂, Al₂O₃-TiO₂, Al₂O₃-ZnO, Co-TiO₂ and N₂-TiO₂ have been prepared and studied for structural, surface, optical and chemical properties [2-6]. Surface oxygen vacancies play an important role in the properties of such binary oxide thin films. Binary oxide thin films are exploited for various applications such as photo-catalytic activity, gas sensors, solar cells and ferroelectrics [7-10], optical switches [11], and integrated devices [12]. Pseudo binary oxide films have been prepared by many methods such as spin coating [13], chemical evaporation method [14], electro-deposition technique [15] and spray pyrolysis technique [16, 17]. We have chosen spray pyrolysis technique for the preparation of pseudo binary oxide thin films, as this technique is reported to be good for mass production of good quality films on large area at a lower cost [18]. In this work pseudo binary oxide thin films of (TiO₂)_{1-x}(Al₂O₃)_x with various mole fractions were successfully prepared by spray pyrolysis technique under optimum condition, such as the distance between the spraying head and hot substrate is 30cm, the compressed air pressure was maintained at 4.5 Kg/cm² and deposition temperature 300°C [18]. The obtained films were characterized by X-ray diffraction for structural properties and phase transformations as a result of change in molar fraction of binary oxides. The chemical composition and surface morphology were analyzed by EDAX and SEM. Optical studies were made by employing UV-vis. spectrophotometer and various optical parameters were estimated. In structural properties of pseudo binary oxide films mixed phase transformation were obtained. Optical properties of Al₂O₃-TiO₂ thin films were studied in wavelength range 350nm to 1200nm, both transmission and reflectance spectra were recorded and analyzed for the optical parameters, such as refractive indices, optical dielectric constant and thickness of pseudo binary oxide films.

2. Experimental

Pseudo binary oxide (TiO₂)_{1-x}(Al₂O₃)_x thin films were prepared by spray pyrolysis technique on cleaned quartz and silicon substrates. 0.1 M of Aluminum acetyl Acetate (C₁₅H₂₁AlO₆) was prepared dissolving in Dimethyl formamide (C₃H₇NO) solvent as Al source. 0.1 M of Titanium (IV) Isopropoxide (C₁₂H₂₈O₄Ti), as Ti source, was prepared by dissolving in absolute ethanol (C₂H₅OH) and Acetyl Acetone (C₅H₈O₂) was used as a complexing agent. The prepared solutions were mixed thoroughly in appropriate volume which is calculated from the atomic fraction or molar fraction formula, as defined as $x = \{(\text{Al}_2\text{O}_3) / ((\text{Al}_2\text{O}_3) + (\text{TiO}_2))\}$ for varying 'x' values, i.e. x=0, 0.1, 0.2, 0.3, 0.4 and 0.5. Before deposition the substrates were cleaned properly. Quartz substrates were cleaned first with soap solution then by Chromic acid followed by acetone and finally De-ionized water, dried with hot air. Silicon substrates were cleaned by three steps, first RCA-1, RCA-2 [19] and finally HF solution. Then cleaned substrates were loaded inside the spray chamber where the spraying head was placed down facing the hot plate 30cm away from the substrate. The structural properties of pseudo binary oxide and un-doped TiO₂ thin films were studied by X-ray diffractometer using Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$) (RIGAKU-MINIFLEX-II desktop). For the optical studies, the transmission and reflectance spectra were investigated using UV-Vis spectrophotometer (OCEAN OPTICS HR4000) in the wavelength range of 350 to 1200 nm. The surface morphology was studied using Field emission scanning electron microscope (ULTRA 55, Karl Zeiss).

3. Results and Discussion

3.1. X-ray diffraction

X-ray diffraction spectra of the pseudo binary oxide thin films are shown in Fig.1. The XRD patterns show diffraction peaks at $2\theta = 25.25^\circ (101)$, $38.57^\circ (112)$, $48.075^\circ (200)$, $53.89^\circ (105)$, $55.06^\circ (211)$, $62.68^\circ (204)$ and $70.309^\circ (220)$, and their position and relative intensities are quite consistent with the standard JCPDS pattern (Card No. 21-1272) which also confirm the formation of anatase phase. The XRD pattern of Al₂O₃-TiO₂ film (Fig. 1) show an additional diffraction peak at $2\theta = 18.37^\circ (002)$ corresponding to the mixed phase of Al₂TiO₅ (Aluminum Titanium oxide) and in agreement with JCPDS pattern (Card no. 74-1759). The diffraction peak observed at $2\theta = 15.48^\circ (200)$, corresponds to the Al₂O₃ phase and is in good agreement with the JCPDS pattern (Card no. 86-1410). It can be observed that with the increase in Al₂O₃ content the peak intensity of XRD at $2\theta = 70.309^\circ (220)$ of Al₂O₃-TiO₂

films gradually diminish due to the formation of mixed phase. It is interesting to see that, the diffraction peak at $2\theta = 25.25^\circ$ (101) is not detectable in Al_2O_3 - TiO_2 films, this attributed to the Al_2O_3 - TiO_2 films have higher grain size than the TiO_2 film, this result has also been observed from the SEM.

Fig. 1 X-ray diffraction of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various x values.

3.2. SEM and EDAX

Fig. 2 (a, c, e, g, i and k) shows the Scanning electron microscope (SEM) micrographs of pseudo binary oxide thin films $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ as a function of molar fraction (x). SEM micrograph shows spherical grains with nano porous surface and some clusters, it is also composed of crumb like nano particles. The average grain size, as estimated from SEM micrographs, are found to be 60.8 nm, 64.14 nm, 105 nm, 144.3 nm and 149.5 nm corresponding to increase in Al_2O_3 content, i.e. molar fraction $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 , respectively. The grain size found to increase with the increase in Al_2O_3 content, which may be attributed to the highly porous compact nature of Al_2O_3 than TiO_2 thin films [20]. Fig. 2 (b, d, f, h, j, l and n) show the Energy Dispersive X-ray analysis (EDAX) which provide Chemical composition and elemental details in atomic percentage. In the EDAX spectrum, the signals corresponding to oxygen (O_2), titanium (Ti), aluminium (Al) and substrate silicon (Si) are seen, elemental analysis shows that the atomic and weight percentage are in stoichiometry ratio as shown in Fig. 2 (b, d, f, h, j, l and n). Strong silicon peak which appear in the spectrum might be due to the smaller thickness of films as compared to the substrate thickness. From the micrograph it is observed that with the increase in the Al_2O_3 content in thin films, the aluminium atomic and weight percentage increase and EDAX also shows good stoichiometry ratio of elements inside the films.

3.3. Optical Study

Fig.3 shows the plot of transmittance versus wavelength of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films, the obtained transmittance spectra was recorded in normal incidence in the wave length range of 350-1200 nm. It can be observed from the transmission spectra that the TiO_2 film possesses more than 80% transmittance which is attributed to the lower porosity in films. As observed from the transmittance spectra of TiO_2 thin films, increase and decrease behaviour of transmission with increase in wavelength might be due to the scattering of light by neighbouring particles which causes the constructive and destructive interference. With increase in the Al_2O_3 contents the transmittance decrease, this may be due to absorption of large amount of light by pores and grains inside films.

Fig. 2 SEM (a, c, e, g, i and k) and EDAX (b, d, f, h, j and l) spectrograph of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various x values.

Fig. 3 Transmittance versus wavelength of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various x values.

Fig. 4 Reflectance versus wavelength of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various x values.

Fig. 4 shows the reflectance spectra as a function of wavelength, the reflectance were recorded in normal incidence by using UV-Visible Spectrophotometer at a wavelength range of 350-1200 nm. It is observed that with the increase in Al_2O_3 content the reflectance decreases, this may be due to the increase in surface roughness and formation of nano pores inside the films which lead to large amount of absorption of light. In reflectance spectra, maximum and minimum peaks are observed, with these peaks the thickness and refractive index of the films were estimated [21] employing the equations (1) and (2), estimated values are tabulated in table-1.

$$n = \sqrt{n_o n_s \left(\frac{1 + \sqrt{R_p}}{1 - \sqrt{R_p}} \right)} \quad (1)$$

$$t = \left(\frac{\lambda_1 \lambda_2}{4(n(\lambda_1)\lambda_2 - n(\lambda_1)\lambda_2)} \right) \quad (2)$$

Where n_o is refractive index of air ($n_o=1$) and n_s is the refractive index of the silicon substrates ($n_s=3.4$), R_p is maximum reflectance value. The thickness of the films were calculated, value are found to be, 96nm, 99.66nm, 105nm, 112.0nm, 136nm, and 138nm, , 96nm and corresponding to (pseudo binary oxide thin films) $x=0.0$ (undoped TiO_2 thin films), 0.1, 0.2, 0.3, 0.4, and 0.5, respectively as shown in Table 1. With increasing Al_2O_3 contents the thickness of the films increases, this attributed to the increasing grain size of the films.

Table-1 Optical parameters of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films

Molar fraction	Thickness (nm)	Energy band gap (eV)
$x=0$	96	3.51
$x=0.1$	99.66	3.58
$x=0.2$	105	3.61
$x=0.3$	112	3.65
$x=0.4$	136	3.68
$x=0.5$	138	3.74

Using the experimental transmittance data of Al_2O_3 - TiO_2 thin films the refractive index (n) and extinction coefficient (k) were estimated. These are also called as real and imaginary part of refractive indices in complex form i.e., $n^*=n-ik$. Fig.5 and 6 shows the refractive index and the extinction coefficient of the Al_2O_3 - TiO_2 thin films. The equations (3), (4) and (5) were used for the calculations. It can be observed from Fig 5 that the refractive index increase with increase in Al_2O_3 content in the thin films, which may be due to the increase in grain size that in-turn

enhance packing density. The refractive index decrease with increase in wavelength, this is attributed to mixed phase of obtained films. Fig. 6 shows that the extinction coefficient increase with increase in Al_2O_3 content, this due to the increasing porous structure of the films. The following expressions have been used [22].

$$n = \left[N + \left(N^2 - n_s^2 \right)^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad (3)$$

$$\text{Where } n_s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{\frac{1}{2}} \quad (4)$$

$$N = \frac{1}{2} \left(1 + n_s^2 \right) + \frac{2n_s(T_M - T_m)}{T_M T_m} \quad (5)$$

Where T_s is the measured transmittance of the quartz substrate in the absence of the TiO_2 film, T_M and T_m are transmittance of maxima and minimum of the TiO_2 thin films, respectively.

$$k = \frac{\left(2.303 \log_{10} \left(\frac{1}{T} \right) \right) \lambda}{4\pi t} \quad (6)$$

Where T is the transmittance of the TiO_2 film and t is the thickness of the TiO_2 film. The complex dielectric constant of the thin films is described as [23]. $\varepsilon = \varepsilon_r + \varepsilon_i$, where ε_r , ε_i are the real part and imaginary part of dielectric constant respectively, these relation can be expressed as.

$$\varepsilon_1 = n^2 - k^2 \quad (7)$$

$$\varepsilon_2 = 2nk \quad (8)$$

The complex dielectric constant of the thin films can be expressed as $\varepsilon = \varepsilon_r + \varepsilon_i$, where ε_r and ε_i are the real and imaginary part of dielectric constant, respectively, and are described in equation (7) and (8). It can be observed from the Fig. 7 and 8 that, the real and imaginary part of dielectric constant increases with increase of Al_2O_3 content; this may be attributed to the increased dielectric nature of the film as well as the increased porosity.

The absorption coefficient has energy dependence near the absorption band edge and its dependence on photon energy is expressed as [24]

$$(ah\nu) = A(h\nu - E_g)^{\frac{1}{2}} \quad (9)$$

Where A is a constant, $h\nu$ is the photon energy and E_g is the optical band gap. The absorption coefficient has energy dependence near the absorption band edge and its dependence on photon energy is expressed as (9). The plot shows the $(ah\nu)^2$ versus $h\nu$ in Fig. 9. The estimated values are tabulated in table-1. It is observed that, with the increase in molar fraction the energy band gap changes may be attributed to the variation in width of the localized states and also formation of mixed phase as seen from XRD pattern [25]. Due to defects in the deposited TiO_2 films, calculation of the Urbach energy is important as it gives the information about the width of the localized states. For the Urbach energy calculations, following empirical relation has been used [26].

$$\alpha = \alpha_0 \exp \left(h\nu - E_g / E_u \right) \quad (10)$$

Where α_0 and E_g are the constants. It states that the absorption coefficient (α) near the fundamental absorption edge is exponentially dependent on the incident photon energy.

Defects are rich in the deposited TiO_2 films, calculation of the Urbach energy is important as it provides the information about the width of the localized states. For the Urbach energy calculation (10) empirical relations were used. From the slope $E_u = \left(d(\ln(\alpha)) / d(h\nu) \right)^{-1}$ of $\ln(\alpha)$ versus Energy in Fig.10, Urbach energy was calculated. Estimated values are found to be 1337 meV, 1187 meV, 1173 meV, 1170 meV, 1160 meV and 1158 meV corresponding to $x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5 . It can be seen that as the Al_2O_3 content increase the Urbach energy decrease due to the existence of defects inside films.

Fig. 5 Refractive index versus wavelength of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films at various x values.

Fig. 6 Extinction coefficient versus wavelength of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films at various x values.

Fig. 7 Real part of dielectric constant versus wavelength of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various x values.

Fig. 8 Imaginary part of dielectric constant versus wavelength of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various x values.

Fig. 9 $(\alpha h\nu)^2$ versus Energy of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various values x.

Fig.10 $\ln(\alpha)$ versus Energy of $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$ thin films for various x values.

4. Conclusion

Pseudo binary oxide thin films, $(\text{TiO}_2)_{1-x}-(\text{Al}_2\text{O}_3)_x$, were prepared by spray Pyrolysis technique on cleaned quartz and silicon substrates at a substrate temperature of 350 °C. The X-ray diffraction reveals that the obtained films shows anatase phase and mixed phase of aluminium titanium oxide (Al_2TiO_5). The surface morphology as observed from SEM image shows spherical grains with rough and porous surface structure. The EDAX provides the chemical elemental analysis which reveals that with increase of Al_2O_3 contents, oxygen weight percentage found to decrease. Optical parameters were estimated from optical studies of the TiO_2 - Al_2O_3 films. It is observed that, with the increase in molar fraction there is variation of the energy band gap, which may be attributed to the mixed phase formation in the films as well as formation of defects. The obtained TiO_2 - Al_2O_3 films show porous surface structure; consequently films contain large surface area and are useful for humidity sensing application.

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