Optical Characterization of Synthesized Pure and Copper Doped Titanium Oxide Thin Films

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ABSTRACT

Pure titanium oxide (TiO$_2$) and copper (Cu) doped TiO$_2$ thin films have been deposited on glass substrate by spray pyrolysis deposition technique (SPDT). Titanium chloride (TiCl$_4$) and copper acetate (Cu (CH$_3$COO)$_2$, H$_2$O) were used as source of Ti and Cu. The doping concentration of Cu was varied from 1-10 wt. %. The optical properties of the as-deposited TiO$_2$ thin films have been investigated as a function of Cu-doping level. The optical transmission of the films was found to increase from 88 % to 94 % with the addition of Cu up to 8% and then decreases for higher percentage of copper doping. The optical band gap for pure TiO$_2$ film is found to be 3.40 eV. Due to Cu doping, the band gap is shifted to lower energies and then increases further with increasing of the concentration of the dopants. The optical conductivity has been found to be for 8wt. % Cu (CH$_3$COO)$_2$, H$_2$O + 92 wt. % TiCl$_4$ is 3.00 eV. The refractive index of the films is found 2.5825 and the variation of refractive index is observed due to Cu concentrations. It is evident from the present study that the Cu doping promoted the film morphology and also its optical properties of the films.

Keywords: Ti, Cu, band gap, SPT

1. INTRODUCTION

Experimental work on thin films has been continued in different parts of the world for successful applications of their properties in scientific, engineering and industrial purposes. The increasing demands for microelectronics and micro structural components in different branches of science and technology have greatly expanded the sphere of thin film research [1] – [3]. Transparent and conducting oxides (TCOs) are extensively used for a variety of applications including architectural windows, solar cells, flat-panel displays, smart windows, and polymer-based electronics.

This can be achieved by the development of transparent and conducting oxide (TCO) coatings such as tin oxide (SnO$_2$) [4], zinc oxide (ZnO) [5], Nickel oxide (NiO) [6], and Titanium oxide (TiO$_2$) [7]. From these materials, Titanium oxide shows unique characteristics in chemical inertness, stability to heat treatment and mechanical hardness. The present research work aimed at the production of uniform, conductive pure and Cu doped tin oxide thin films by a low cost technique using precursor solution of TiCl$_4$. There are many techniques, including spray pyrolysis, sputtering, evaporation and solgel, by which thin films may be deposited on glass substrates [8] – [12]. In this study, TiO$_2$ thin films were prepared by the spray pyrolysis technique which is particularly attractive because of its simplicity, fast, inexpensive, and suitable for mass production [13]. The optical band gap varies from 3 eV > 3.4 eV as a function of oxygen/argon ratios in the flowing gas between 10% to 50% of TiO$_2$ thin films prepared by DC Magnetron Sputtering method [9].

2. EXPERIMENTAL DETAILS

Pure TiO$_2$ and TiO$_2$:Cu films were deposited using homemade spray pyrolysis technique (SPT) coating unit. The quality of these films depends on various process parameters such as spray rate, substrate temperature and the ratio of the various constituents in the solutions. 0.1M of TiCl$_4$ was added with 50 ml water and 50 ml ethanol for precursor solution for pure TiO$_2$ thin film. (1-10) wt % of Cu (CH$_3$COO)$_2$, H$_2$O was dissolved in TiCl$_4$ solution for Cu doped thin films deposited. To enhance the solubility of prepared solution, a few drops of HCl were added. The transparent solution thus obtained and subsequently diluted by ethanol, served as the precursor. The distance between substrate to nozzle was 25 cm. air pressures was 1 bar, spayed time was 5 min. and spray rate was kept constant. For each concentration the reproducibility of the films were verified by repeating the experiments several times. Microscope glass slides, cleaned with organic solvents, were used as substrates. The main reaction may be leads to the formation of TiO$_2$ as

$$\text{TiCl}_4 + \text{O}_2 (g) \rightarrow \text{TiO}_2 (s) + 2\text{Cl}_2 (g) \uparrow .$$

And the possible reaction for formation of Ti$_x$Cu$_{1-x}$O thin films on heated substrates may leads to

$$\text{TiCl}_4 + \text{Cu} \ (\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O} + \text{O}_2 (g) \rightarrow \text{(Ti}_x\text{Cu}_{1-x})\text{O} \downarrow + \text{CH}_3\text{CO}_2 \uparrow$$

The thickness of the thin films was measured by the setup of Fizeau fringes method. The transmission and absorption spectra for the as-deposited films were recorded using a S-3400N HITACHI, JAPAN. UV-VIS-IR spectrophotometer as a function of wavelength ranging from 300 to 1100 nm.

3. RESULTS AND DISCUSSION

The objective of this study is to synthesis and characterization of pure and Cu doped TiO$_2$ thin films by home fabricated spray pyrolysis system. The colour of the
pure TiO$_2$ thin film is white (deep) which turns grays white on copper doping. In looking the film is uniform and homogeneous. The thickness of the films was varying with ±10 nm, but here films were used for measurement only whose films thickness was about 200 nm.

Transmission spectra were taken within range of 300 nm to 1100 nm for films. Fig. 1 shows the variation of transmittance with wavelength for pure and Cu doped TiO$_2$ thin films. It is seen from the graph that the values of transmittance is high in the visible and IR region it is minimum at wavelength ~ 300 nm. Films prepared at 350° C exhibit a transmission of > 60% in the visible and IR region, again it is found > 70% in the visible and IR region for Cu doped film, which is found to be greater than that of undoped film. It is found that transmittance decreases with increasing concentration of the dopant, which is due to the increase in the amorphous nature of the doped films. The transmittance of the films is also influenced by a number of effects, which include surface roughness and optical inhomogeneity in the direction normal to the film surface.

The absorption coefficient is of the order of 10$^6$ m$^{-1}$ which may also be suitable for a transparent conducting film. From both the figures it is observed that the absorption coefficient first increases slowly in the low energy region i.e. in the high wavelength region and then increases sharply near the absorption edge. The value of the absorption coefficient depends on Cu doping. It is decreases as the concentration of Cu increases but it is increases as Cu doping as more than 8%. Significantly, it was observed that at a dopant concentration of ~ 8 wt% the transmittance in the films reached a minimum accompanied by increase in the optical band gap. At the same value of dopant concentration the resistivity also reached a peak. This behavior appears to be a consequence of valence fluctuation in Ti between the 2$^+$ and 4$^+$ states. The transparent conductivity behavior it’s a model that attributes presence of Ti interstitials rather than oxygen vacancies alone in the presence of Ti$^{2+}$. Fig. 2 shows the variation of absorption with wavelength of pure and Cu doped thin films. It is found that the absorption is decreased with higher wavelength slowly. It is also observed that absorption is increases rapidly at lower wavelength. For Cu doping up to 8%, absorbance shifted to low intensity but more than 8% of Cu doped it shifted to high intensity compared to pure TiO$_2$ thin films. The absorbance spectrum for pure and Cu doped TiO$_2$ thin film is shown in Fig. 5, absorbance spectrum shows low absorbance in the entire wavelength region but it high at wavelength < 350 nm. This reduction of absorbance in Cu doped samples can be explained as due to the removal of defects and disorder in the as-deposited film by Cu doping. The important optical characteristic of TiO$_2$ film is that they are transparent in the wavelength ranging from 400 to 1100 nm. At wavelengths shorter than 400 nm, absorption occurs due to the fundamental band gap, and thus light cannot be transmitted due to quantum phenomenon. At longer wavelengths, reflection occurs because of the plasma edge, and light cannot be transmitted due to a classical phenomenon. The corresponding wavelengths for those transmissions are determined by a number of fundamental characteristics as well as by the concentration of free electrons. The optical band gap (E$_g$) is determined from the plots of ($\alpha h\nu$)$^2$ vs. photon energy (h$\nu$) for direct transition of pure and Cu doped SnO$_2$ thin films as shown in fig. 3. The direct band gap energy of the films have been obtained from intercept on the energy axis after extrapolation of the straight line section of ($\alpha h\nu$)$^2$ vs. h$\nu$ curve. The variation of band gaps for Cu doped is shown in fig. 4. The direct band gap of pure TiO$_2$ thin films obtained 3.40 eV which is an excellent agreement with the reported value of band gap determined by others workers. For 8% Cu doping the direct band gap of the film becomes 3.20 eV. So it is clear that for Cu doping change the direct band gap of the pure TiO$_2$ thin films. These values are small compared to the reported values. The variations of refractive index for pure and Cu doped TiO$_2$ thin films statesman are graphically shown in Fig. 5. The refractive index of pure TiO$_2$ thin film have been obtained 2.58 which values is very close to the reported values 2.6 to 2.55 and lowest refractive index become 2.45 for 8% Cu doping. The observed value is low compared to the reported values for similar films [14]. As suggested by Arai [15] this low value of refractive index may probably due to the smaller density of the films. It is observed that refractive index increases further than Cu doped. At the films shows high index because the impurity in the film increases optical properties. The reason is that, at high temperature the mechanism of impurities thermal activation becomes the dominant one. It is seen from the graph that the transmittance decreases with copper (Cu) doping up to 8% once more transmittance increases. The decrease of transmittance means increase of band gap with temperature may due to the increase of carrier mobility or due to increase of carrier concentration. So it is clear that beyond 8% Cu doping for more carrier concentration exists such that scattering occurs and then band gap increases. The excess of Cu atoms do not occupy the popper lattice positions to contribute to the free carrier concentration while, at the same time, enhance the disorder of the structure leading to an increase in band gap. This is expected as the periodicity of Ti matrix distributed in the film in presence of Cu atoms might enhance the scattering of the conduction electrons.

On increasing the concentration of Cu the band gap of the Cu doped thin film decreases were further increased of the band gap of the Cu thin film due to the decrease in the atomic density in these planes. This process leads to the movement of Ti$^{4+}$ ions in the interstitial sites and also an increase in the amorphous phase and disorder.
Figure 1: Variation of transmittance as a function of wavelength for pure and Cu (1% to 10%) doped TiO₂ thin films.

Figure 2: Variation of absorption coefficient with respect to wavelength for pure and Cu (0-10%) doped TiO₂ thin films.

Figure 3: Variation of \((a\hbar^2/c)^2\) with photon energy for pure and Cu (1-10%) doped TiO₂ thin films.

Figure 4: Variation of direct band gap of pure and Cu doped TiO₂ thin films with Cu.

Figure 5: Variation of refractive index of pure and Cu doped TiO₂ thin films with Cu doping.

4. CONCLUSION

Spray pyrolysis is a suitable and novel technique for the production of quality TiO₂ thin films. TiO₂ films were successfully prepared on glass substrates by spray pyrolysis technique. The average thickness of the film is found to be 200 nm. The pure TiO₂ films have good optical transmission and it is about 88%. Maximum transmission about 94% is found for 8% Cu doped TiO₂ films but beyond 8% Cu doped, transmission decreases.

The direct band gap of pure TiO₂ thin film is reduced after Cu doping. The UV-vis spectrum shows the optical band gap of TiO₂ thin films to be 3.40 eV and after Cu doping it is reduced which is in good agreement with theoretical values. The refractive index of the pure films is bring into being 2.5825 and for 8% Cu doped TiO₂ thin film is 2.4525. The thin films with good optical transparency are to be prepared with 8 wt% Cu doping.
For Cu doping resulted in the extension of absorption edges of TiO$_2$ films from UV region to visible light region. The photo catalytic activity of TiO$_2$ thin film has been investigated. Optical transmittance spectra for the Cu-Ti-O thin films reveals that all the films demonstrate more than 80% transmittance at wavelengths longer than 500 nm and absorbance is high in the ultraviolet region.

REFERENCES


