Variation of Optical and Electrical Properties of Zr Doped TiO₂ Thin Films with Different Annealing Temperatures

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Abstract. Zr doped (0.01M) TiO₂ thin films were fabricated by unconventional sol-gel technique starting from powder precursors. Using microscopic glass slide, the films were deposited and annealing was done at different temperatures. In order to study the structural properties of these fabricated films x-ray diffraction has been adopted. Similarly, for the study of optical and electrical properties, UV-VIS spectrophotometer and Hall measurement techniques have been adopted for all the fabricated samples. It is found that the doped TiO₂ thin film annealed at 350 °C showed a reduced band gap value in comparison to other films. This sample is also found to have highest optical and electrical conductivity which makes it suitable for light harvesting. Our result shows that Zr doped TiO₂ thin film annealed at 350 °C plays an important role in tuning the properties for device applications.

1. Introduction

Doping metal oxides is one of the ways of improving the properties of oxides for its suitable use in electronic devices. Doping of transition metals induce changes in structural characteristic, optical as well as electrical properties of the parent metal oxide. TiO₂ is the most frequently studied metal oxide due to its non toxicity, low cost and various applicability starting from photo-catalysis to gas sensing [1-2]. TiO₂ is not efficient enough to use the solar energy effectively and hence is its main demerit. So, in the past decade a lot of metal and non metal doping is done and investigated systematically to enhance the visible –light response and photocatalytic activity under visible light irradiation[3-5]. Zr has same valence state as that of Ti as both of them are same subgroup elements. So Zr⁺ doped TiO₂ has attracted interest of many researchers. ZrO₂ has a good dielectric and optical properties due to which it finds several applications in gas sensors and parts of batteries [6-7]. Recently it has been reported that doping small amount of Zr improved the surface property of TiO₂ and thermal stability of anatase phase and thereby increased the photocatalytic activity [8-9]. In this present work TiO₂ has been doped with low concentration Zr⁺ ions (0.01%M) and were prepared by unconventional sol-gel techniques and annealed at different temperatures. Several optical properties of the thin films were studied in detail and their effect on annealing temperature.
2. Experimental

2.1 Sample preparation: TiO₂ powder (99.9%) pure, and ZrO₂ powder (Merck), Acetic acid, Nitric acid were used as the starting materials. Calculated quantities of precursor materials were mixed in acetic acid. The solution was continuously stirred until a lump free and uniform paste was formed. Hydrolysis of the paste was carried out by drop wise addition of DI water with continuous stirring. The process continued till a clear sol was obtained. The sol was vigorously stirred at 500rpm with a magnetic stirrer almost for about an hour which was followed by refluxing with 0.1M nitric acid. During this step continuous stirring was done at a temperature of 180°C. The process continued almost 8-9 hours until the gel was formed. The wet gel was deposited on the clean microscopic glass slide by doctor blade technique. Then the films were annealed at the temperature range from 300-400°C.

2.2 Characterization: The X-ray diffraction (XRD) pattern of all the films were acquired on a Brucker AXS D8 Advance diffractometer (CuKα, λ=1.54Å)The data were recorded in the angular range 20-80° with step size 0.02° and scan speed of 0.6s. The transmittance and reflectance data for normal incidence was taken in the wavelength range 300-900nm by the UV-Vis photo spectrometer (Cary 5000). Filmetrics-F-10 was used to measure the thickness of all the fabricated films and Ecopia HMS-3000 was used to measure the electrical conductivity and Hall mobility.

3. Results and discussions

3.1 Structure: The XRD spectra of all the synthesized Zr doped TiO₂ thin films after being annealed at different studied temperatures are shown in Figure 1. All the films are polycrystalline films. The crystal structure of the films are tetragonal body centered with space group I41/acd. The crystallite size of all the planes corresponding to maximum intensity are calculated by Scherrer formula[10] and is presented in Table 1. It is found that the crystallite size goes on increasing with annealing temperature which can be interpreted by Arrhenius law given as[11]

\[ D = D_0 e^{-E_a/RT} K_0 \]  

(1)

![Figure 1(a) The X-ray diffractogram of Zr+ doped TiO₂ thin films](image)
From this the activation energy is calculated which is found to be 0.08 eV which is very much close to that of anatase form. The diffraction peaks of the Zr+ doped TiO2 films are located at the same angle(=26°) for all annealing temperature which indicates that the Zr+4 ion exists in TiO2 in substitutional mode.

TABLE 1: Variation of crystallite size with annealing temperature

| Annealing temperature in °C | Crystallite size in nm |
|-----------------------------|------------------------|
| 0                           | 48.57                  |
| 300                         | 67.989                 |
| 350                         | 67.997                 |
| 400                         | 68.001                 |

3.2 Optical Properties: From the absorbance, transmittance and reflectance data, the different optical parameters like absorption coefficient ($\alpha$), energy band gap ($E_g$) and refractive index ($n$) are calculated by using the given formulae

$$\alpha = \frac{\ln (\frac{I}{I_0})}{d}$$  \hspace{1cm} (2)

where $T$ is the transmittance of the film and $d$ is the thickness of the film. The band gap is calculated by Tauc plot method by plotting the graph between $\theta$ and $(\alpha \theta)^2$ [12]. The calculated value of the band gaps are presented in Table-2. It is found from fig-2 that the band gap for the film annealed at 350°C is the lowest indicating that it is the most efficient film for light harvesting. The refractive indices of the films are calculated by using the formula [13]

$$n = \frac{1 + R^{0.5}}{1 - R^{0.5}}$$  \hspace{1cm} (3)

where $R$ is the normal reflectance of the films at different wavelengths. Figure 2(b) shows the refractive index variation as a function of wavelength of the incident radiation. It is observed that the refractive index of the film annealed at 350°C is the highest.
The optical conductivity, which determines the optical response of the material is determined by the formula given as

$$\sigma_{opt} = \frac{\varepsilon \pi n c}{4\pi}$$  \hspace{1cm} (4)$$

where $n$ is the refractive index of the material and $c$ is the velocity of light. The optical conductivity in different photon energy region is shown in fig -3 which indicates that the film...
annealed at 350°C has highest optical conductivity over the whole spectral domain as compared to other films. As we know optical conductivity is related to electrical conductivity in presence of alternating field so the optical conductivity is compared with the electrical conductivity of the films obtained from Hall measurement. Figure-3(b) shows that conductivity of the film annealed at 350°C is the highest. The mobility of the same sample is also highest. But we know that mobility is affected by collision of charge carriers and scattering. As temperature increases the mobility due to phonon scattering decreases and due to high thermal velocity of electrons the scattering also decreases. But here the increase in mobility may be due to the dominance of ionized impurity scattering at 350°C which also supports the reduction in band gap at the same annealing temperature.

Figure 3(a) The optical conductivity of Zr+ doped TiO2 thin films

Figure 3(b) The variation of electrical conductivity of Zr+ doped TiO2 thin films with annealing temperature
TABLE-2 Variation of band gap and mobility with annealing temperature

| Annealing temperature in °C | Band gap in eV | Mobility in cm²/Vs |
|-----------------------------|---------------|--------------------|
| 0                           | 3.24          | 8100               |
| 300                         | 3.73          | 22.5               |
| 350                         | 3.07          | 9460               |
| 400                         | 3.99          | 37.9               |

Conclusion:

Zr⁺ doped TiO₂ thin films are prepared by unconventional sol-gel method and its optical and electrical properties are studied at different annealing temperatures. The optical band gap of the film annealed at 350°C is the lowest. The same film also has the highest refractive index. The optical as well as the electrical conductivity of film annealed at 350°C is highest which may be considered as the most suitable for harnessing the most part of solar radiation.

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