Optical and electrical properties of sol-gel spin coated titanium dioxide thin films

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Abstract. In this work; TiO$_2$ thin films were deposited on glass and stainless steel substrates by sol-gel spin coating method. The films deposited on glass were annealed at different temperatures ($T_a$) in the range of 200 to 500 $^\circ$C and that are deposited on steel substrate were annealed at 800 $^\circ$C. The optical properties of TiO$_2$ thin films were studied by using UV-VIS spectroscopy and photoluminescence (PL) spectroscopy. The transmittance on the average was found to $\geq$ 80 % and is found to sensitive to $T_a$. The PL spectra exhibited the strong emission band associated with band- to- band transition around 390 nm and the two weak bands at 480 and 510 nm associated to the oxygen defects and surface defects respectively. The current-voltage (I-V) characteristics of the Al/TiO$_2$/steel capacitors were studied and analysed with application of various current mechanisms. Analysis reveals that the conduction in Al/TiO$_2$/steel capacitors is governed by Poole-Frenkel mechanism.

1. Introduction
Thin films of titanium dioxide (TiO$_2$) have been attracted considerable attention due to its wide band gap, high dielectric constant, biocompatibility, thermal stability, strong oxidized stability, good transmittance in the visible region, high refractive index, chemical stability, non-toxicity and long term photo-stability [1-3]. These properties make them potential candidates for many applications ranging from daily cosmetics to microelectronics industry. It is known that TiO$_2$ is exist in three polymorphic forms such as anatase, rutile and brookite. The TiO$_2$ in anatase and rutile phases are widely studied for different applications due to their stability at normal pressures, high refractive index and dielectric constant. Different methods such as pulsed laser deposition, sputtering, electron beam evaporation, solvo thermal synthesis, chemical vapour deposition, electrophoretic and sol–gel process have been employed to fabricate the TiO$_2$ thin films [4-5]. Usually, the sol–gel process is considered as one of the most appropriate technology to prepare thin films due to several advantages such as good homogeneity, ease of composition control, low processing temperature, large area coatings and low equipment cost.
Even though many studies have been reported on TiO$_2$ films from last few decades [6-7] but there is still a need to study the effect of vacancies which are inevitable due to the annealing at high temperatures on the optical and electrical properties of TiO$_2$ films.

In this work, we have studied the effect of annealing temperature on optical and electrical properties of sol-gel spin coated TiO$_2$ films and an attempt has been to correlate them.

2. Experimental Techniques

In this work, the TiO$_2$ films were deposited by sol-gel spin coated method. The sol-gel of TiO$_2$ is prepared as follows. Titanium isopropoxide [Ti(OCH(CH$_3$)$_2$)$_4$] (Sigma-Aldrich, 97%) which is a liquid at room temperature, was used as the organometallic (OM) precursor and 1 ml of it was added into propanol by a glass dropper in a closed environment in order to avoid the contact with moisture. The solution was stirred for 15 minutes. Then Glacial Acetic acid (Emplura, 99-100%) (2.8 ml) was poured into it. The solution remains yellow transparent and stirring is continued for 15 minutes in closed environment. During the stirring methanol (Sigma-Aldrich, 99.8%) (2 ml) was added drop wise and stirring is continued for 2 hours in closed environment. Two drops from the solution was taken and spin coated on clean glass substrate using the Spektrospin spin coater with the spinning speed of 2000 rpm for a duration of about 2 minutes. The same procedure was adopted to coat the TiO$_2$ films on stainless steel substrate. The samples deposited on the glass were annealed in the temperature range of 200-500 $^\circ$C and the samples deposited on the stainless steel were deposited at 800 $^\circ$C. The transmittance properties of TiO$_2$ thin films were recorded using Agilent UV-Vis spectrophotometer with diode array detector and the photoluminescence spectra were recorded using Perkin Elmer Fluorescence Spectrometer (Model No.-LS 55) at room temperature.

3. Results and discussion

The emission spectra were recorded in the wavelength of 350 nm to 600 nm at an excitation wavelength of 330 nm and is shown in figure 1 for the samples annealed at 200, 300 and 500 $^\circ$C.

![Figure 1: Photoluminescence spectra of the TiO$_2$ films annealed at different temperature](image-url)
All the spectra exhibited one strong and two weak bands. The strong band aroused around 397, 384 and 376 nm respectively for films annealed at 500, 300 and 200 °C. This strong band arises due to the transition of electrons from conduction band to valence band and the energy corresponds to this peak can be taken as the energy gap of TiO$_2$ [8]. The second weak emission peaks occur at 473, 482, 479 nm respectively. This peak can be attributed due to oxygen vacancy in TiO$_2$ film and is in good agreement with literature. The third emission peaks are located at 513, 508, and 510 nm. This green band is attributed to the surface defects [9]. It is observed from the figure 1 that with increase in the annealing temperature, the peak intensities increase. So, it may be inferred that with increase in temperature, crystalline nature of the films increases and enhances the photoluminescence emission. Further, the emissions correspond to the defects also increases as annealing temperature increases. The transmittance versus wavelength plot for TiO$_2$ thin films were shown in figure 2.

![Transmittance spectra of sol-gel coated TiO$_2$ films annealed at different temperatures](image)

Figure 2: Transmittance spectra of sol-gel coated TiO$_2$ films annealed at different temperatures

From the figure 2 one can observe that transmittance of the films is above 81% for the films annealed at in the temperature range of 200 to 400 °C. The high transmittance region on a wide range of wavelength in the visible region (from 352 to 650 nm) has been observed and can be used in the applications of solar cells. The films annealed at temperature of 500 °C show the less transmittance value as compared to the other films. Usually decrease in transmittance can be attributed to the increases in thickness or high defect concentrations. Since all the films deposition and annealing conditions are same, the low transmittance can be attributed to the high defect concentration as evidenced by PL spectra.

The current-voltage (I-V) characteristics of the Al/TiO$_2$/stainless steel capacitor were studied in configuration of metal-insulator-metal (MIM) configuration at room temperature. Forward bias was applied from +5 to -5 V and reverse bias was applied from -5 to +5 V. The bias was applied to the top
Al contact while the bottom contact was kept at the ground potential. I-V characte\-ris\-es of the film Al/TiO$_2$/stainless steel capacitor is shown in figure 3(a).

They exhibit a slight asymmetric nature which could be different metal electrodes. Based on the value of magnitude of current, we can confirm that the films are good semiconductor. To analyse the I-V curves different current conduction models including the space charge limited conduction mechanism; Schottky and pool-frenkel mechanism were considered. For P-F conduction mechanism, the electric current is described as follows [10]

\[
\ln(I) = \left(\frac{e}{kT}\right) \sqrt{\frac{\varepsilon_0 \varepsilon_r d}{kT}} \cdot \sqrt{V}
\]

Where \( V \) is the applied voltage, \( e \) is the electronic charge, \( \varepsilon_0 \) -electric permittivity of free space, \( \varepsilon_r \) -permittivity of film, \( k \)-Boltzmann constant, \( d \)-thickness of film. The \( r \) is a coefficient ranging from 1 to 2 depending upon the exact position of the Fermi level. For \( r=1 \), the conduction mechanism is called normal P-F mechanism and for \( r=2 \), it is called trap filled P-F effect.

![Figure 3(a) I-V characteristics and (b) Poole-Frenkel plot for -5 to 0 V at negative bias.](image)

The slope was obtained from the liner fit of the plot as shown in figure 3(b) and the relative permittivity of the film was estimated from equation (1). The refractive index (n) was found to be 2.45 which is in good agreement with the value of standard Anatase phase of TiO$_2$. Therefore P-F mechanism governs the conduction mechanism in TiO$_2$ films where oxygen vacancies are act as traps as evidenced by PL properties.
4. Conclusions
This work highlighted the photoluminescence, transmittance, and electrical properties of TiO$_2$ thin films were prepared by sol-gel, spin-coating method and subsequently annealed at different temperatures. The PL spectra of the films exhibited one strong peak and two weak peaks associated to band-to-band transition and defects. The transmittance characteristics revealed that the TiO$_2$ films are transparent and the transmittance value ≥ 80 % in the visible region. I-V analysis suggests that, Poole-Frenkel mechanism governs the conduction in the present films and the validity of this model was verified by estimating Refractive index and is in good agreement with the standard value of Anatase phase of TiO$_2$ films.

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