Screen printed TiO₂ film: A candidate for photovoltaic applications

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Abstract

In this paper we report synthesis and analysis of low cost screen printed coating of TiO₂ in the form of thick film fabricated on glass substrate followed by annealing at 350 °C. The film has been characterized by x-ray diffraction (XRD), Scanning electron microscope (SEM) with energy dispersive x-ray (EDX), UV-visible and Fourier-transform infrared (FTIR) spectroscopy and current-voltage (I-V) measurement via two probe. The XRD analysis showed that the prepared thick film has crystal structure of anatase phase with preferred orientation of (1 0 1) plane. The SEM image identified porous nature of film while EDX spectra revealed the presence of titanium and oxygen atoms in the film. The FTIR spectrum displayed the strong presence of TiO₂. DC electrical conductivity measurements revealed that electrical conductivity increases on increasing temperature which confirms semiconducting behaviour.

1. Introduction

Over the past decade, research on semiconducting films have been pursued with growing interest on account of their established and useful applications for optoelectronics [1–3]. These films possess wide range of characteristic properties such as high resistivity and stability, which make them perfectly suited for novel applications such as heat reflecting windows, photo thermal, photovoltaic and environmental purification [4]. Titanium dioxide (TiO₂) is a class of wide band gap semiconductor with band gap 3.2 eV and has received significant amount of interest because of possessing good insulting properties, high transmittance and refractive index in the visible range, which makes this material useful for various industrial applications, namely white pigments for paints, fillers, battery electrodes, photo-induced water splitting, gas sensors, dye-sensitized solar cell (DSSC) [5]. In addition, TiO₂ film shows high performance due to long electron diffusion length and a pronounced light scattering effect, leading to an efficient harvesting of sunlight [6]. Various methods have been reported for synthesis of TiO₂ thin films including chemical vapour deposition [7], sol-gel process [8], spray pyrolysis [9], hydrothermal method [10], e-beam evaporation [11], laserdeposition technique [12] and Screen printing [13]. Out of these techniques, Screen printing method has many advantages over the other ones, such as simple equipment, low cost, ecofriendly and for large area deposition at room temperature.

Previous investigations of the microstructural as well as optical properties of TiO₂ films that were prepared by Chemical Bath Deposition (CBD) technique have shown tremendous performance. Similarly, screen printed TiO₂ based DSSCs show highly efficient performance which also depends on the paste compositions [14]. Based on this fact we report the synthesis and the characterization of TiO₂ screen printed film, which is based on dispersion of TiO₂ paste on glass substrate. The prepared films were characterized for their structural, surface morphology, optical properties and electrical studies. The results of the characterization studies are discussed in the paper for photovoltaic application.

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2. Experimental technique

Merck-made Analytical Reagent (AR)-grade Titanium dioxide (TiO₂) white powder, anhydrous Titanium tetrachloride (TiCl₄) and ethylene glycol (C₂H₆O₂, 99.99% purity) have been used for the fabrication of TiO₂ thick film following standard procedure of screen printing method [15]. In this method TiO₂ and TiCl₄ were mixed with few drops of ethylene glycol to convert it into a paste for the fabrication of thick film as described in [16]. A description of screen printing process is depicted in figure 1. During deposition process, the screen is placed a few millimetres above the surface of the substrate and the paste is dispersed through squeegee (doctor blade) [17]. In this way screen printed TiO₂ thick film is produced. The film is then sintered under muffle furnace at 350 °C in order to remove the organic compounds completely [18].

3. Characterization techniques used

X-ray diffraction pattern was recorded by using Bruker AXS D8 Advance x-ray diffractometer at 2θ position (from 20° to 80°) with Cu Kα x-ray (λ = 1.54056 Å). EDS and SEM characterizations were carried out by using SEM (JEOL JSM-7600F) at 5 kV accelerating voltage. UV–vis spectrometer (Hittachi-3400) was used for absorbance measurement in the 300–900 nm wavelength range. IR transmission spectrum was recorded by FTIR spectrophotometer (SHIMAZU-8400S) in 3500–500 cm⁻¹ range. The thickness of film was calculated with the help of gravimetric weight difference method and that comes out to be in micron. The DC resistivity measurement was done by using standard two probe technique (Keithley electrometer-6517A).

4. Results and discussions

4.1. X-ray analysis

Figure 2 shows the XRD pattern of TiO₂ thick film sintered under muffle furnace at 350 °C. The XRD pattern in general exhibited high degree of crystalline nature. The crystalline phase present in this film was identified as anatase structure of TiO₂ as shown inset in figure 2. The identified peaks (101), (002), (200), (105), (211), (204), (116), (220), and (107) matches well with JCPDS Card No.86115 [10]. A pronounced (1 0 1) peak of TiO₂ at 25.23° was observed. This peak corresponds to the tetragonal anatase phase and was used for obtaining the structural parameters. The size of the particle present in TiO₂ thick film was calculated by using the famous Debye–Scherrer formula as shown in equation (1),

\[ G = \frac{k \lambda}{\beta \cos \theta} \]

where G is the particle size(nm), \( \lambda \) is wavelength of x-ray beam(1.54 Å), k is shape factor (0.94), \( \beta \) is full width at half maximum (FWHM) of the most intense peak, and \( \theta \) is the diffraction (Bragg) angle. The calculated particle size was found to be 19.93 nm from the most intense peak(101). In fact, the synthesis mechanism involves dislocation of particles which are imperfections. The dislocation density can be evaluated from the particle size (G) by the relation given in equation (2) and is found 2.52 \( \times 10^{11} \) line m⁻². These values are in good agreement with the reported ones [19].

\[ \delta = \frac{n}{G^2} \]

where, n is a factor, which equals unity for minimum dislocation density.
While the lattice constants for the tetragonal structure is determined by the below relation.

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}.
\]  

From the above relation the cell constants for anatase phase are found to be \(a = 3.7687\ \text{Å}\) and \(c = 9.5024\ \text{Å}\), which are well consistent with the reported cell constants for TiO\(_2\) [19].

### 4.2. Surface morphology and elemental composition

SEM image of TiO\(_2\) screen printed film on glass substrate is shown in figure 3(a). Small grains with dense structure, full surface coverage and the distribution of grains on entire surface are almost agglomerated throughout the surface areas clearly seen.

Energy dispersive spectroscopy (EDS) characterization is a useful technique to determine the percentage of various individual elements in a compound material. In this research EDS image of screen printed TiO\(_2\) film confirmed the presence of Titanium and Oxygen only and is shown in figure 3(b). The average atomic mass percentage of TiO\(_2\) as revealed from EDS were 45.32% and 54.68%, respectively, and this shows that the film is nearly stoichiometric with the initial amount of TiO\(_2\) compound. While as other peaks may be attributed due to Au/Pt coating on substrate.
4.3. Optical analysis

The basic principle of UV–vis spectroscopy is excitation of electrons from the ground states to different excited states of the absorbent. The absorbance, transmittance and reflectance spectra versus wavelength for TiO₂ screen printed film are shown in figures 4(a) and (b) in 300 to 700 nm range, respectively. From the absorbance data, we can calculate transmittance (T) as well as reflectance [20].

\[ T = 10^{-A} \]  

where \( T \) is Transmittance and \( A \) is absorbance of the film then, reflectance of the film can be calculated by using following equations as,

\[ R = 1 - (T \times e^A)^{1/2} \]  

The light absorbing property of a material is related to the absorption coefficient (\( \alpha \)). This parameter (\( \alpha \)) can be measured from Beer-Lambert’s law i.e.,

\[ \alpha = 2.303 \frac{A}{t} \]  

where \( A = \) absorbance, \( t = \) film thickness.

From the absorption coefficient, one can calculate energy band gap of the material in the UV region by using Tauc’s relation [21].

\[ \alpha h \nu = B(h \nu - E_g)^n \]  

Here, \( B \) is constant, \( h \) is Planck’s constant, \( \nu \) is frequency of incident photon, \( E_g \) is optical band gap and the exponent represents type of transition. From equation (7), the direct gap of the material can be calculated and that comes out to be 3.25 eV as shown in figure 5. This value is quite suitable for photovoltaic devices.

4.4. Fourier transform infrared spectroscopy analyses

FTIR was used for the analysis of chemical changes in the modes of vibration and bond nature of the material that is deposited in the form of film. Figure 6 represents the FTIR spectra recorded in the wavelength range 500–3100 cm\(^{-1}\) for the TiO₂ thick film. In this spectra the bands observed at 3300 and 1400 cm\(^{-1}\) were assigned to the presence of –OH group of water absorbed and hydroxyl group on the surface. The weak bands observed around 1840 and 2335 cm\(^{-1}\) were due to the bending vibration of the –OH bond of chemisorbed water and the band observed around 3045 cm\(^{-1}\) called H–O–H antisymmetric stretching mode is due to adsorbed moisture/water [22]. The narrow band around 2903 cm\(^{-1}\) is due to organic residues and strong band observed at about 655 cm\(^{-1}\) confirms the vibration mode which is the characteristics of semi-crystalline anatase phase for TiO₂ [23].

4.5. Electrical conductivity mechanisms

Electrical conductivity is the capacity of a material to conduct an electric current when an electrical potential difference is applied across it and movable charges start flowing, giving rise to an electric current. From figure 7,
Figure 5. Tauc plot of TiO₂ screen printed film.

Figure 6. FTIR spectra of TiO₂ screen printed film.

Figure 7. I-V behaviour of TiO₂ screen printed film.
the current (I) grows exponentially as the voltage (V) increases and this growth is the signature of increase in electrical conductance and this may be due to decrease in potential barrier. The current-voltage (I-V) variation is non-linear and the reason for this non-linear behaviour may be that the film consists of ionizing impurity levels and agglomeration of grains as depicted from SEM.

The conductivity of TiO₂ film can be measured as follows [24]:

\[ R_S = \frac{4.532}{I} V \]

where, \( R_S \) = sheet resistance (resistivity = \( \rho \)), 4.532 = correction factor, \( V \) = voltage measured and \( I \) = the current applied from the test unit. Thus, electrical conductivity can be determined by;

\[ \sigma = \frac{1}{\rho} \]

where, \( \sigma \) = electrical conductivity. The variation of conductivity (\( \sigma' \)) with temperature is explained by Arrhenius equation given by:

\[ \sigma = A \exp\left(\frac{-E_a}{KT}\right) \]

where \( A \) is the pre exponential factor, \( E_a \) is the activation energy, \( K \) is the Boltzmann constant and \( T \) is the temperature in Kelvin. For thermally activated band conduction, the resistivity (\( \rho \)) can be expressed as:

\[ \rho = \rho_0 \exp\left(\frac{E_a}{KT}\right) \]

where \( \rho_0 \) is the parameter that depends on sample.

It has been observed that both resistivity (\( \rho \)) and conductivity (\( \sigma \)) versus 1000/T curve are inter-related in which resistivity decreases with temperature while conductivity increases with respect to temperature indicating semiconducting type of behaviour which is shown in figure 8. In this study, electrical conductivity measurements of titanium dioxide thick film was carried out in a temperature range of 280–390 K and is found to be \( 8.3 \times 10^{-7} (\Omega^{-1} \text{ m}^{-1}) \) at 300 K in an open atmosphere. The activation energy is found to be 0.23 eV for screen-printed TiO₂ film. Thus, our sample shows high value of conductivity and low activation energy as compared to the reported value by Pomoni K et al [25]. This is due to the fact that decreasing of activation energy is the result of weakened potential barrier.

The improvement in both optical and dark conductivity of TiO₂ sample was observed in rare-earth oxide’s doped TiO₂ samples [26, 27]. Since electrons from the rare-earth oxide’s valence band or photoexcited f-states are donated to fill the deepest gap states, reducing the trapping probability and improving both light and dark conductivity. This in turn provides an explanation for the improved performance of REO doped titania LCD, LED, solar cells and etc.

Figure 8. Arrhenius plot of resistivity as well as conductivity of TiO₂ screen printed film.
5. Conclusion

Screen printing is obviously versatile technique and has great importance in the fabrication and application of optoelectronic devices. TiO$_2$ is one of the most promising photovoltaic materials for fabricating solar cell and other hetero-junction based material devices revealed from the results. From XRD results we infer that the TiO$_2$ particles are intertagonal anatase phase with dislocation density and lattice parameters investigated by using the same XRD data. Porous surface morphology was identified from SEM image and proper elemental compositions were detected by EDS. Direct band gap of 3.25 eV was obtained from absorbance data. FTIR spectra confirmed the TiO$_2$ stretching and hydroxyl group in the TiO$_2$ sample. The semiconductor behaviour was observed from both resistivity and conductivity DC measurement. This type of work speaks of the possibilities of novel applications in which material deposited via screen printing can be used to produce optical and electronic devices.

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