Fabrication and Characterization of TiO$_2$ Thin Films and n-TiO$_2$/p-Si Junction Diodes via Dip Coating Technique

R. Rajeswari $^{a,*}$, D. Venugopal $^a$, P. Jayabal $^a$ and A. Dhayal Raj $^b$

$^a$Department of Physics, Gobi Arts & Science College, Gobichettipalayam, Erode 638452, Tamil Nadu, India
$^b$Department of Physics, Sacred Heart College, Tirupattur 635 601, Tamil Nadu, India

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The structural and electrical properties of as-prepared and calcinated TiO$_2$ thin films prepared using the dip coating method are studied. The thin films are deposited by different dip cycles. Subsequently, the samples are used for a p–n junction diode application at room temperature. The films are characterized by XRD, SEM, EDX, UV–Vis spectroscopy, FTIR and $I$–$V$ to understand the structural and electrical properties. The XRD pattern reveals that the TiO$_2$ thin films deposited at ambient temperature are amorphous and the films annealed at 450 $^\circ$C with different dipping cycles are polycrystalline in nature with tetragonal structure. The surface seems to have a uniform sphere-like morphology, with the diameter of ca. 20 nm that is observed from the SEM micrographs. The EDX spectrum confirms the presence of titanium and oxygen in the samples. The electrical behavior of the thin films is studied and it represents that the obtained maximum average conductivity is $10.68 \times 10^{-12}$ S/cm for the annealed TiO$_2$ thin films. The diode measurements are taken in darkness and under halogen light. The diode parameters such as ideality factor ($n$) and barrier height ($\Phi_b$) are calculated using the J-V method.

1. Introduction

The semiconducting transition metal oxides (TMO) are well-known candidates for p–n junction diodes. The physical, chemical, optical, electrical and other properties of the oxide semiconductors can be modified very comfortably as per essentiality by directly tuning a band gap through morphology, doping impurities, ohmic contact formation, etc. [1–3]. Also — due to the longitudinal heterojunction interface, related oxygen vacancies, interstitial defects and strong light trapping [4, 5] on the front panel of the optoelectronic devices — these metal oxides attracted special interest of researchers. Among a variety of semiconducting TMOs, such as TiO$_2$, ZnO, Fe$_2$O$_3$, SnO$_2$, etc., the TiO$_2$ semiconductors have become dominant materials in the field of thin film research due to relatively easy construction methods, higher efficiency [6–8] and their semiconducting nature stemming from their band gap energy.

Recently, titanium dioxide (TiO$_2$) has gained great significance because of its high thermal stability, high dielectric constant, high refractive index, large band gap and low leakage current density. It possesses potential for use in p–n junction diodes, antireflection coating, solar cell catalysis and sensors [9]. In point of fact, TiO$_2$ has been applied in solar cells [10], diodes [11], gas sensors [12], electrochromic [13] and photochromic batteries [14], pseudo capacitors [15] and in the biomedical field [16]. Formerly, TiO$_2$ has been synthesized by different techniques such as sputtering, electron beam evaporation, chemical vapor deposition, sol-gel method [17, 18], etc. Among them, the sol-gel dip coating technique has been recruited to grow ultra-thin and high dielectrics on a substrate. This technique has such advantages over other deposition methods as excellent thickness uniformity over large substrate areas, low processing temperature, low impurity content and completely precise thickness control [19, 20].

In our experiment, TiO$_2$ thin films are prepared using the dip coating method with different dip cycles. Structural and electrical properties of the prepared films are studied using different characterization techniques such as XRD, SEM, FTIR, etc. Further, the p–n junction is formed by taking the TiO$_2$ as a n-type material on p-type silicon and the fabricated p-Si/n-TiO$_2$ junction diode characteristics are studied in darkness and under the illumination of a halogen lamp with the use of the J-V method.
2. Experimental procedure

2.1. Materials

Titanium tetra isopropoxide (TTIP, 97%) was purchased from Sigma-Aldrich, dimethylformamide (DMF, 99%), nitric acid (HNO₃, 69%), deionized water, absolute ethanol (C₂H₅OH) and acetylacetone (CH₃COCH₂COCH₃) were purchased from Merck. All chemicals are used as received without further purification.

2.2. Preparation of TiO₂ thin films and fabrication of n-TiO₂/p-Si diode

TiO₂ thin films are synthesized by the sol-gel dip coating technique with high precision while maintaining a high optical quality. Titanium (IV) isopropoxide (TTIP) is used as a precursor to prepare TiO₂ sol. A mixture of N–N dimethyl formamide (DMF), ethanol and acetyl acetone is added to titanium (IV) isopropoxide and then diluted by adding a mixture of ethanol and water under continuous magnetic agitation at room temperature. One drop of HNO₃ is added five times for every 10 min to the above-mentioned mixture. The colour of the solution changes from white to transparent TiO₂ sol. The native oxide on the polished surface is removed by applying the HF+H₂O (1:10) solution.

Once the cleaning process is completed, the Si wafer is ready for a coating process. A similar film formation procedure is carried out for the coating of TiO₂ layer on the Si wafer instead of the glass substrate (see Sect. 2.2) and then annealed at 450°C for 1 h. After the annealing, a better ohmic contact has formed by using the Ag paste. The Ag paste is applied on both surfaces in order to get good solderability, high electrical conductivity, low sheet resistance and good adhesion. Now, the device is dried at room temperature for 5 h for further investigation. Hereafter, the as-deposited samples are named as d, while the annealed samples with 5, 10 and 15 dip cycles are named as d₅, d₁₀ and d₁₅, respectively.

3. Results and discussion

3.1. X-ray diffraction pattern

Figure 1 shows the XRD pattern of as-deposited and annealed TiO₂ thin films. The d₅, d₁₀ and d₁₅ samples calcinated at 450°C show the diffraction peaks designating the high crystalline nature of pure TiO₂ thin films. All the diffraction peaks are well-matched with the anatase phase of TiO₂, without any mixed phase like rutile. The positions of the diffraction peaks are in good match with those given by JCPDS Card No. 21-1272 [21] with the lattice constants area: \( a = 3.782\,Å \), \( b = 9.513\,Å \) and \( c = 2.513\,Å \). Thus, the formation of pure TiO₂ with tetragonal structure is confirmed. However, the peaks are comparatively broad due to the small size of the crystals. The Debye-Scherrer equation is used to determine the average crystallite size by peak broadening analysis. The anatase film with grain sizes of 7.93 nm, 8.01 nm and 8.18 nm is obtained for d₅, d₁₀ and d₁₅ samples for (101) plane, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>glass</td>
</tr>
<tr>
<td>dipping speed</td>
<td>190.00 mm/min</td>
</tr>
<tr>
<td>lifting speed</td>
<td>190.00 mm/min</td>
</tr>
<tr>
<td>length</td>
<td>25.0 mm</td>
</tr>
<tr>
<td>wet time</td>
<td>6 min</td>
</tr>
<tr>
<td>dry time</td>
<td>3 min</td>
</tr>
<tr>
<td>cycles</td>
<td>5, 10 and 15 cycles</td>
</tr>
<tr>
<td>pre-annealing time</td>
<td>30 min</td>
</tr>
<tr>
<td>pre-annealing temp</td>
<td>150°C</td>
</tr>
<tr>
<td>post-annealing time</td>
<td>1 h</td>
</tr>
<tr>
<td>post-annealing temp</td>
<td>450°C</td>
</tr>
</tbody>
</table>
3.2. Morphological analysis

Figure 2 shows SEM images of as-deposited and calcined TiO₂ thin films. The as-deposited sample d seems to have a smooth surface without any cracks. The d₅ and d₁₀ samples show some cracks appearing on the surface of the films. In case of the d₁₅ sample, the surface is very smooth, uniform and crack-free which might be due to the effect of coating cycles. The crack-free d₁₅ sample does not only lack cracks or any other defects in the coatings but its structure and morphology are also more perfect. The surface seems to have a uniform sphere-like morphology, with the diameter of ca. 20 nm [22].

The prepared thin films are subjected to EDX analysis to work out the chemical compositions of the samples. Figure 3 depicts the EDX spectra of as-deposited and annealed thin films. It is very clear that the elemental composition of all the samples consisting of Ti and O indicates the absence of other elemental impurities. The at% and wt% of the samples are shown in Table II. The O–Ti ratio is calculated as 2.8, 2.7, 2.5 and 2.4 for d, d₅, d₁₀ and d₁₅, respectively. From the elemental composition table, it is confirmed that there is an excess of oxygen present in the sample during the preparation. Moreover, the other high intense peak present in the EDX spectra is due to the silicon substrate [23].

3.3. Optical analysis

The UV–Vis absorption spectrum of as-deposited and annealed TiO₂ thin films is shown in Fig. 4. The optical absorption spectra of all the samples in the UV region are due to the wide band gap nature of TiO₂. The absorption edge in the UV region is due to a band to band transition. The optical absorption properties of the semiconductors are related to the energy band gap and the same properties are estimated by the UV–Vis absorption spectra. The optical band-gap E₀ of the semiconductor materials is calculated as follows:

\[(\alpha h\nu)^n = A (h\nu - E_0)\],

where \(\alpha\), \(\nu\), \(E_0\) and \(A\) are the absorption coefficient, light frequency, band gap energy and absorption constant, respectively, and \(n\) depends on the characteristics of the transition in a semiconductor. Here, \(n\) is equal to 1/2 as the material is an indirect-band gap semiconductor.
In Fig. 5 the intersection point between the extrapolation linear portions gives the value of the energy band gap $E_g$ [24]. The optical band gap of the TiO$_2$ thin films is estimated as 3.65, 3.41, 3.23 and 3.08 eV for d, d5, d10 and d15, respectively. The estimated band gap value is decreased when the dip cycle is increased. This decrease in the band gap for the d5, d10 and d15 samples is due to the increase in the grain size of the deposited films [25-27].

3.4. Functional group analysis

The vibration behavior of the bonds present in the prepared samples has been investigated through FTIR. Figure 6 shows the FTIR spectra of the as-deposited and annealed TiO$_2$ thin films. The absorption bands located at 633 cm$^{-1}$ and 566 cm$^{-1}$ for as-deposited and annealed TiO$_2$ thin films samples are assigned to the Ti–O vibration. This indicates the formation of pure TiO$_2$ in as-prepared films as well as in the annealed films. The other bands are due to the absence of stretching and bending vibrations of hydroxyl groups and these bands are reduced for the annealed samples [28].

3.5. $I$–$V$ characteristics

The current-voltage ($I$–$V$) measurement is performed by using a 2-point probe connected to a source meter of Keithley Electrometer 6517 B. The $I$–$V$ characteristics of TiO$_2$ thin films are tested at six different temperatures: room temperature, 40, 60, 80, 100 and 120°C. In Fig.7 one can see the current-voltage ($I$–$V$) characteristics of the d and d15 TiO$_2$ thin films. Current values of the synthesized thin films are measured in the voltage range 10–100 V. It can be clearly observed that the current values increase linearly with the applied voltage while all the samples satisfy Ohm’s law [29].

The relation between the electric field strength $E$ (V/m) vs current density $J$ (A/cm$^2$) for the TiO$_2$ thin films one can see in Fig. 8a, while in Fig. 8b the relation between $\sqrt{E}$ vs ln($J$) is presented. These graphs are plotted only for samples tested at 120°C for d and d15 TiO$_2$ thin films.
Electrical parameters obtained from $I$–$V$ characterization

<table>
<thead>
<tr>
<th>TiO$_2$ annealing temperature</th>
<th>Current at 120$^\circ$C for 100 V [A]</th>
<th>Conductivity $\sigma$ [s/m]</th>
<th>Resistivity $\rho$ [Ω m]</th>
<th>Current density $J$ [A/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>$5.93 \times 10^{-10}$</td>
<td>$5.96 \times 10^{-12}$</td>
<td>$1.67 \times 10^{11}$</td>
<td>$2.60 \times 10^{11}$</td>
</tr>
<tr>
<td>d15</td>
<td>$1.46 \times 10^{-09}$</td>
<td>$10.68 \times 10^{-12}$</td>
<td>$0.93 \times 10^{11}$</td>
<td>$4.66 \times 10^{11}$</td>
</tr>
</tbody>
</table>

Fig. 8. (a) Electric field vs current density and (b) $E^{1/2}$ vs ln J of TiO$_2$ thin films.

When the electric field increases, the current density also linearly increases, and for both the films it becomes more linear [30]. The current density and electric field are calculated from the $I$–$V$ graph.

Furthermore, electrical conductivity $\sigma$ (S/m) of TiO$_2$ thin films is found to increase gradually with the increase in annealing temperatures, see Fig. 9. Electrical conductivity of prepared samples is calculated as in [31]. Also, it is found that the increase in annealing temperature decreases the electrical resistivity $\rho$ (Ω m).

Figure 9 shows the average electrical conductivity and resistivity of TiO$_2$ thin films.

On the other hand, the resistivity of thin films decreases as the annealing temperature increases [32]. The as-deposited TiO$_2$ thin film has the highest resistivity of $1.67 \times 10^{11}$ Ω m, whereas the annealed TiO$_2$ thin film has the lowest resistivity of $0.93 \times 10^{11}$ Ω m. This improvement of conductivity and current density for the annealed sample is due to the increase of grains size and mobility of charge carriers within TiO$_2$ thin films [33]. Moreover, a very low value of electrical conductivity is due to the excess amount of oxygen present in both samples which is confirmed by the EDX spectra. The oxygen content in the sample determines the value of conductivity in the sample. Samples with oxygen vacancies form titanium suboxides leading to higher conductivity [34]. However, here the process is contrary to the oxygen vacancy which produces no titanium suboxides. Also, in the case of the d sample, there is more excess oxygen so that conductivity is lower as compared to the annealed d15 sample. The increase of the annealing temperature causes a reduced oxygen content and leads to higher conductivity in the d15 sample, as compared to the d sample.

3.6. The diode characterization of n-TiO$_2$/p-Si

The p–n junction diode is fabricated by the p-type Si with n-type TiO$_2$ and their functions are calibrated in darkness and under a halogen light source. Figure 10a shows the $I$–$V$ characteristics of the diode and Fig. 10b shows the semi-logarithmic plot for the current density ln(J) vs voltage $V$ that is represented as the J-V method. The negative top electrode of the devices is represented as the forward bias direction of the current. Measurements from +4 to −4 V bias voltage correspond to the forward to reverse current. The good rectification behavior is observed for the n-TiO$_2$/p-Si diodes. Note,
The influence of light it decreases to 10.55. This n-TiO value for p-type silicon is 32 A/(cm K) varies by material and doping. The theoretical emission theory as follows [36]:

\[ J = J_0 \exp \left( \frac{qV}{nk_B T} - 1 \right) \]

where \( J_0 \) is the reverse saturation current, \( q \) is the electron charge, \( V \) is the applied voltage, \( n \) is the ideality factor, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The ideality factor \( n \) and the reverse bias saturation current \( J_0 \) of the diode are determined from the slope. In turn, the intercept of the semi-logarithmic forward bias \( J-V \) plot for \( V \geq 3k_B T/q \) using (1) and the ideality factor \( n \) and the barrier height \( \Phi_b \) can be calculated as follows [37]:

\[ n = \frac{q}{k_B T} \frac{dV}{d \ln(J)}. \]

\[ \Phi_b = \frac{k_B T}{q} \ln \left( \frac{A^* T^2}{J_0} \right) \]

where \( A^* \) is the Richardson constant. This value varies by material and doping. The theoretical value for p-type silicon is 32 A/(cm K)^2 [38].

Using the J-V method, the \( n \) value for n-TiO/p-Si diode is 13.29 in darkness but under the influence of light it decreases to 10.55. This device can be used in solar cells because the increase in luminescence improves the ideality factor. The barrier height \( \Phi_b \) value for n-TiO/p-Si diode is 0.24 eV in darkness but under the light it interestingly increases to 0.38 eV. It is clear that the increase in luminescence improves the barrier height for the system indicating that the diodes can be used in optoelectronic devices. The obtained ideality factor values are more than one (\( n = 1 \) for an ideal diode). The non-idealities are due to the presence of a bias-dependent barrier height, the existence of the interfacial thin native SiO2 layer between the metal (Ag contact) and semiconductor (Si wafer) or generation-recombination currents within the space charge region [39]. Other reasons may be due to the states associated with the defects near the surface of the semiconductor [36, 40], chemical reactions and barrier inhomogeneities [35].

4. Conclusion

The as-deposited and annealed TiO2 thin films are prepared using the sol-gel dip coating technique. XRD results showed the formation of a pure anatase phase with a tetragonal structure. The SEM analysis reveals that the surfaces of thin films are uniform for 15 dip cycles with a sphere-like morphology. The average diameter of the particle is ~20 nm. The EDX spectra indicate the composition with excess oxygen present in the samples. The optical band gap value of the thin films is decreased with the increase of the dip cycle. After annealing, the decrease in the band gap is observed and it can be directly connected to the increase in the structure ordering as observed in the XRD results. The functional analysis reveals that the Ti-O-Ti bands have the tendency to become narrow with the increase of the annealing temperature. This may be due to the breaking of Ti-O-Ti bonds when the annealing temperature increases. The prepared films exposed the semiconducting nature seen in the \( I-V \) plot which is favorable for electronic and optoelectronic applications. The ideality factor \( n \) and barrier height \( \Phi_b \) values are \( n = 13.29, \Phi_b = 0.24 \) eV in darkness and \( n = 10.55, \Phi_b = 0.38 \) eV under light illumination, respectively obtained for the fabricated n-TiO2/p-Si diode.

References


