Synthesis and study of reflectance and transmittance of a transparent conducting oxide: Niobium (Nb) doped Titanium dioxide (TiO$_2$) at different doping concentrations

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Abstract—In this paper we have successfully prepared the Niobium (Nb) doped Titanium dioxide (TiO$_2$) thin film with different Nb doping concentration. There are many methods for the synthesis of Nb doped TiO$_2$ thin films such as sputtering, pulsed laser deposition, chemical vapour deposition, sprays pyrolysis and sol-gel methods. But here Nb doped TiO$_2$ thin films were coated on glass substrate by sol-gel spin coating technique. Diffused reflectance and transmittance has been studied with different doping concentration. We have measured diffuse reflectance of Nb doped TiO$_2$ thin films by taking different Nb concentrations with the help of Diffuse Reflectance Spectrometer (DRS). It is clear there are differences in the position of the absorption edge. It is observed that the total reflectance for Nb doped TiO$_2$ thin film changes with increasing the Nb concentration. The experimental results indicated that the optimum concentration is 5wt. % and can be used to obtain Nb doped TiO$_2$ thin films with a very high transmittance (88.5 %). We observed different absorption edge at different wavelength which depends on the doping concentrations. The samples showed a better transmittance in the visible region and a sharp fall in the UV region. The increase of the surface roughness leading to decrease of the peak values.

Keywords—Doping, Reflectance, Transmittance, thin films, Sol-Gel method

I. INTRODUCTION

Transparent conductive oxides (TCO) are the oxides of metals having high electrical conductivity, high free carrier density and high optical transmittance in the UV/VIS/NIR spectrum. The development of transparent conducting oxides (TCOs) is responsible for generation of many electronic devices such as touch panels, flat panel displays (FPDs), and Si-based solar cells [1-2]. TCOs also play an important role in electronic devices like organic light-emitting diodes (OLEDs), blue GaN-based LEDs and copper indium gallium diselenide (CIGS) solar cells. There is a strong demand of TCOs in the industry for its use in optoelectronic devices. The use of TCO improves the performance of optoelectronic devices. By the use of a TCO whose refractive index similar to GaN would increase the external quantum efficiency of blue Light Emitting Diodes [3]. The TCOs with a high transmittance in the infrared region is used to improve the efficiency of solar cells [4]. TCOs are used in a number of electronic devices including Liquid crystal displays, OLEDs, photovoltaic and touchscreens. A TCO is a wide band-gap semiconductor that has a high concentration of free electrons in its conduction band. There are different types of known TCOs such as Indium doped Tin oxide, Aluminium doped Zinc oxide, Fluorine doped Tin oxide and Titanium Dioxide. Titanium dioxide (TiO$_2$) is known over the last few years because of its unique physical and chemical properties, which have a huge applications such pigments, catalysis and sensors [5-6]. Recently TiO$_2$ has been popular as an electronic material, and research work is done for using it as a high-$k$ material and also in resistive random access memory (RRAM) devices [7-8]. Another type diluted magnetic semiconductors of TiO$_2$ have been used in room temperature spin tronic [9]. Reviews works done on properties of TiO$_2$ with respect to its applications is done[10-11]. Among the many types of TiO$_2$, the important crystal structures are rutile and anatase. The rutile structure has been known as a good transition metal oxide. Its electronic structure, optical and transport properties have been studied. Both rutile and anatase tetragonal symmetry, is known as a part of TiO$_2$ octahedral. For the anatase structure, each octahedron is connected with 8neighbours (4 sharing edges and 4 sharing corners), and the rutile has10 neighbours (2 sharing edges and 8 sharing corners).
Ti$_{1-x}$Nb$_x$O$_2$ (TNO) as TCO material has attracted attention because of its properties like high refractive index (~2.7), high transmittance in the infrared region, transmittance of the visible spectrum (above 90%), high thermal & chemical stability in reducing atmosphere, good mechanical hardness, non-toxic materials used, reproducibility and good surface morphology. In this paper we have successfully fabricated the Nb doped TiO$_2$ thin film with different Nb doping concentration. Nb doped TiO$_2$ thin films were coated on glass substrate by sol-gel spin coating technique. Diffused reflectance and transmittance has been studied with different doping concentration.

This paper has been written into five distinct sections—Introduction, Structural Analysis, Experimental procedure, Results and discussion and conclusion. Introduction section gives brief review of literature related to present work done. Structural analysis gives structural study of Titanium dioxide. Experimental procedure gives the method used for the synthesis of Titanium dioxide by sol-gel spin coating technique. Results and discussion section gives the results drawn in this paper. Conclusion part gives the major conclusion drawn here.

II. STRUCTURAL ANALYSIS

Titanium dioxide (TiO$_2$) is equivalent to an ideal semiconductor for photocatalysis because of its properties like low cost, high stability and is safe for both humans and the environment. TiO$_2$ has a higher mobility in comparison to rutile, is more suitable as a main material of TCO. It has large band gap (3.2eV) and low effective mass equivalent to mass of free electron mass. TiO$_2$ is a semiconductor having band gaps of 3.2eV for the anatase, 3.02eV for the rutile, and 2.96 eV for the brookite phases [12]. The valence band of TiO$_2$ has 2p orbitals of oxygen with the 3d orbitals of titanium and the conduction band has 3d orbitals of titanium [13]. When UV or near UV light is incident on TiO$_2$ then electrons from the valence band are transferred to the conduction band leaving holes. The excited electrons in the conduction band are in a 3d state and because of different parity, the transition probability of electrons to the valence band decreases resulting to decrease in the probability of electrons and holes recombination [14]. Anatase structure of TiO$_2$ is the active photo-catalytic component. The properties of TiO$_2$ are improved by doping it with some of the transition metal ions (Fe, Mo, Zr, Nb, V, Sb, W etc.). TiO$_2$ can be made from n or p type semiconductor which is determined by nature of dopant. The ionic radius of Nb$^{5+}$ of 0.061 nm is comparable to that of Ti$^{4+}$ which is 0.060 nm; therefore, Nb$^{5+}$ can act as an n-type dopant in TiO$_2$ crystal lattice and produces excess carriers in the conduction band.

III. EXPERIMENTAL PROCEDURE

There are many methods used for synthesis of Nb doped TiO$_2$ such as Sputtering, Pulsed Laser Deposition, Molecular Beam Epitaxy, Chemical Vapour Deposition, Spray Pyrolysis and Sol-Gel method. We have used here Sol-gel method in our experiment to synthesize Nb doped TiO$_2$ thin films with variation in doping concentration depositing on the glass sides by spin coating technique. The reasons are due to its simplicity, low cost, easy-to-control the process parameters and we can deposit homogeneous film on large substrate area. Our work is focused on the study of the Reflectance and Transmittance properties of Nb doped TiO$_2$ thin films with variation in doping concentration deposited on glass sides by spin coating technique.
SYNTHE
SIS OF Nb DOPED TiO$_2$ THIN FILMS

Titanium (IV) iso-propoxide (TTIP, 98%), Niobium chloride (NbCl$_5$, 99.9%), Hydrochloric acid (HCl, 35%), Ethanol (CH$_3$CH$_2$OH, 99.7%) were first collected. Sol A was prepared by mixing TTIP, Ethanol and HCl in a molar ratio of 1:20:0.2. The above solution was ultrasonically mixed for 12 h at room temperature. Sol B was prepared by first dissolving NbCl$_5$ in Ethanol and then this mixes with HCl with a molar ratio of 20:0.15 followed by sonication for 2 h. An appropriate volume of Sol B was added to sol A and the mixture was stirred for 5 min followed by sonication for 30 min. The final solution contains 1.0 wt% NbCl$_3$.

In the spin coating process, the mixed solution was dropped on a glass substrate spinning at 1000 rpm for 20 s. The coated substrate was dried at 100°C and subsequently annealed at up to 600°C for 60 min in order to crystallized it, Nb doped TiO$_2$ thin films is thus synthesized [9]. Figure 3 shows the steps for deposition of the films.

IV. RESULTS AND DISCUSSION

Measurement of diffuse reflectance with UV-visible spectrometer is a standard technique to study the optical properties of materials. We have measured diffuse reflectance of Nb doped TiO$_2$ thin films by taking different Nb concentrations with the help of Diffuse Reflectance Spectrometer (DRS). It is clear there are differences in the position of the absorption edge. It is observed that the total reflectance for Nb doped TiO$_2$ thin film changes with increasing the Nb concentration. Table 1 shows that the absorption edge shifts to higher wavelengths with the increase in Nb concentrations.

![Flow chart for deposition Nb doped TiO$_2$ thin film](image1)

Figure 3. Flow chart for deposition Nb doped TiO$_2$ thin film

The above solution was ultrasonically mixed for 12 h at room temperature. Sol B was prepared by first dissolving NbCl$_5$ in Ethanol and then this mixes with HCl with a molar ratio of 20:0.15 followed by sonication for 2 h. An appropriate volume of Sol B was added to sol A and the

![Sonication, 180 W, 20 kHz, 12 h](image2)

Sonication, 180 W, 20 kHz, 2 h

![Sonication, 180 W, 20 kHz, 30 min](image3)

Spin coating

Drying, 100 °C, 1 h

Annealing, muffle furnace, 600 °C, 1 h

![Nb DOPED TiO$_2$ FILM](image4)

![Figure 4. Diffuse reflectance curve for Nb doped TiO$_2$](image5)

Figure 4. Diffuse reflectance curve for Nb doped TiO$_2$

Table 1. The obtained values of absorption edge at different values of doping concentration

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Doping Concentration (wt.%)</th>
<th>Absorption Edge (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>315</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>326</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>335</td>
</tr>
</tbody>
</table>

For the transmittance we used a commercial spectrometer that was capable of recording spectra in the visible range as well as in the near infrared and UV rays. Here spectrometer
did not measure the actual values but mainly compare the signal from the sample to a reference beam. Also a baseline was recorded previously to the actual measurements to calibrate the instrument.

Figure 5 shows the transmission spectra of three different samples with different Nb concentration with dependence of the wavelength.

The samples showed a better transmittance in the visible region and a sharp fall in the UV region. The transmittance varies from 88.5% to 60.9% for the samples prepared with different Nb concentration. The increase of the surface roughness leading to decrease of the peak values. The diagram shows that for high energies (lower wavelength) there is no transmission because all the light is absorbed and for low energies (higher wavelength) there are no appropriate electronic transitions possible so transmission is very high in this range. The transmittance spectra show that all the films are transparent in the visible light region and their spectra exhibit a sharp decrease in the UV region because of the light absorption. Film surface roughness and thickness inhomogeneity have a huge effect on the optical transmission spectrum.

Table 2. The values of transmittance at different values of doping concentration

<table>
<thead>
<tr>
<th>Nb doped TiO₂</th>
<th>SAMPLE NO.</th>
<th>DOPTING CONCENTRATION (wt. %)</th>
<th>TRANSMITTANCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>5</td>
<td>88.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10</td>
<td>77.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15</td>
<td>60.9</td>
</tr>
</tbody>
</table>

V. CONCLUSION

In this paper we have successfully fabricated the Nb doped TiO₂ thin film with different Nb doping concentration. Nb doped TiO₂ thin films were coated on glass substrate by sol-gel spin coating technique. Diffused reflectance and transmittance has been studied with different doping concentration. The experimental results indicated that the optimum concentration is 5wt. % and can be used to obtain Nb doped TiO₂ thin films with a high transmittance (88.5 %). We observed different absorption edge at different wavelength which depends on the doping concentrations.

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REFERENCES