# Optical Characteristics of $TiO_2$ Thin Films Sensitized with the Natural Dye of Clitoria Ternatea

Rachel Oommen, P. Usha Rajalakshmi, and S. Sudha

***Abstract*—Thin films of $TiO_2$ are deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) technique. Films are characterized by X-ray diffraction, Scanning Electron Microscopy and UV-Vis. spectrometry. $TiO_2$ films are sensitized by the natural dye extracted from Clitoris Ternatea. Effect of dye sensitization on the optical properties of $TiO_2$ thin films is analyzed. A red shift in the optical band gap of the films is observed upon dye sensitization. The direct and indirect band gap of the sensitized films is in the range of 3.2-3.8eV and 2.0-2.9 eV respectively.**

***Index Terms*—Band gap, clitoria ternatea, dye sensitization, $TiO_2$**

## I. INTRODUCTION

Titanium dioxide ($TiO_2$) is a versatile material and has novel properties suitable for a number of technologically important applications. In addition with the novel properties the material has many advantages such as non-toxicity, high photocatalytic activity, high dielectric constant and it can be synthesized in a cost effective manner. Successive Anionic Layer Adsorption and Reaction (SILAR) method is a deposition technique for making uniform, compact and crystalline thin films .Sensitization of wide band gap materials such as $TiO_2$ and ZnO with the dyes (either natural or artificial) is directed towards the enhancement of optical absorption of the wide band gap semiconductor materials which in turn may lead to improvement of conversion efficiency of photoelectrochemical solar cells. $TiO_2$ is a potential material for dye sensitized solar cells [1]. Hence in the present work it is proposed to sensitize $TiO_2$ thin films with the natural dye extracted from Clitorea Ternatea and to study the effect of dye sensitization on the optical properties of the film. Films are deposited by SILAR method which is based on the successive immersion of the substrate in separately placed cationic and anionic precursors and rinsing between every immersion with ion-exchanged water.

## II. EXPERIMENTAL

In the present work TiCl3 and NH4OH are used as the cationic and anionic precursor respectively for the deposition of $TiO_2$ thin films. Volume percent solutions of cationic and anionic precursors are taken in separate beakers along with distilled water for rinsing after each immersion.

Manuscript received August 7, 2012; revised September 28, 2012.

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2% (volume percent solution) $TiCl_3$ and ammonium hydroxide are found to be optimum for the deposition of $TiO_2$ thin films and films are deposited at different growth rates. Table I depicts the film deposition conditions. The natural dye is extracted from the flowers of *Clitoria Ternatea*, which are rich in anthocyanin. Fresh flowers of Clitoria Ternatea are shadow-dried at room temperature till the flower is completely free from moisture. The dried flower is ground using a mortar and pestle and a coarse powder of the flower is obtained. Ethanol is used as the solvent for extraction of the dye. About 25g of dried powder is mixed with 100 ml of Ethanol and the mixture is kept still for 24 hours under darkness. After 24 hours the solution turned greenish-purple and the dye extract is filtered and used for sensitization of $TiO_2$ thin film. Crystallization of $TiO_2$ thin films is analyzed by PANanlytical X-Pert Pro X-ray Diffractometer. Optical transmittance of the films and optical absorption of the dye extract is recorded using JASCO (V-570) double beam spectrophotometer. The ethanol extract of the dye is analyzed by FTIR spectroscopy. Thickness of the films is determined using mass method.

## III. RESULTS AND DISCUSSION

X-ray diffraction pattern of the as-deposited films and the films annealed at different temperatures is shown in Fig. 1 Absence of peaks in the XRD pattern of the as-deposited film shows that the film is amorphous in nature and consisted of fine grains. No improvement in the crystallinity of the film is observed in the case of films annealed at 300 and 400° C. A broad peak of low intensity at 2θ =25.20° is observed in the case of $TiO_2$ thin film annealed at 500 °C. The peak is indexed by comparing the peak position with the standard data (JCPDS card no. 84-1286). The peak is indexed as (101) plane of anatase phase $TiO_2$ which is a characteristic peak of that phase.

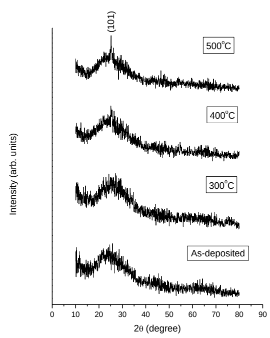


Fig. 1. XRD pattern of as-deposited and annealed $TiO_2$ thin films.

FTIR spectrum of the powder of *Clitoria Ternatea* used for the extraction dye is shown in Fig. 2 the peaks observed at 534.6, 776, 869.34 $cm^{-1}$ may be assigned to Carbonyl deformation, disubstituted aromatic ring, Phenyl ring substitution respectively and the bands at 1083 and 1653 Correspond to $C = O$ stretch (aldehyde). The FTIR spectrum exhibits relevant peaks corresponding to the functional groups present in anthocyanin, which confirm the presence of anthocyanin in the natural dye extracted from

TABLE I: FILM DEPOSITION CONDITIONS.

| Sample | Concentration of precursors | | Adsorption Time (Sec) | Reaction Time (Sec) | Rinsing Time (Sec) | No of SILAR cycles | Thickn-ess (µm) | Growth rate (nm/ Cycle) |
|---|---|---|---|---|---|---|---|---|
| | $TiCl_3$ (Vol. %) | $NH_4OH$ (Vol. %) | | | | | | |
| Sample1 | 2 | 2 | 60 | 60 | 30 | 75 | 0.517 | 6.89 |
| Sample2 | 2 | 2 | 60 | 60 | 30 | 150 | 1.053 | 7.02 |
| Sample3 | 2 | 2 | 60 | 60 | 30 | 225 | 2.341 | 10.4 |

*Clitoria Ternatea*. UV-Vis absorption Spectrum of the natural dye extracted from *Clitoria Ternatea* is shown in Fig. 3. The absorption of the dye is maximum around 600 nm.

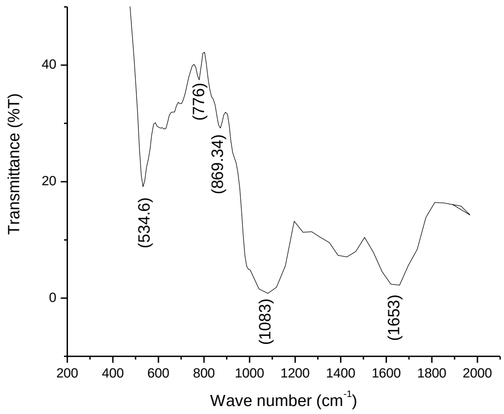


Fig. 2. Ftir spectrum of the *clitoria ternatea* powder.

Optical transmittance spectra of the as-deposited and dye sensitized $TiO_2$ thin film is shown in Fig. 4. (Optical characteristics of sample -1 alone is represented graphically to be brief).The films exhibited high transmittance in NIR region. Transmittance of the films decreases with decrease in wavelength.

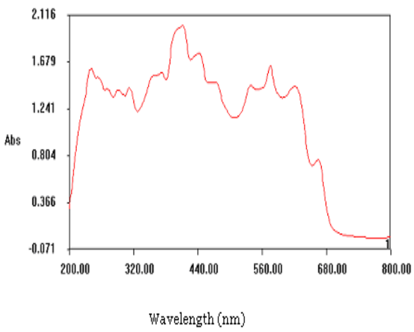


Fig. 3. UV-Vis absorption spectrum of the natural dye extracted from *clitoria ternatea*.

The transmittance of the films fall off rapidly in UV-Vis boundary and the transmittance of the film is negligible in UV-region. The absorption coefficient ($\alpha$) is determined from transmittance ($T$) values using the relation [2]

$$\alpha = (1/t)*\ln(1/T) \quad (1)$$

where't' is the thickness of the film. Absorption spectra of the as-deposited and dye sensitized $TiO_2$ thin films is shown in shown in Fig. 5 Absorption coefficient of the films is very low in longer wavelength region. It increases gradually with increase in wavelength. The films have high absorption coefficient in the short wavelength region .The optical band gap energy of the films is calculated using the classical relationship for near edge optical absorption in semiconductors [3]

$$\alpha h\nu = K\,(h\nu - E_g)^{n/2} \quad (2)$$

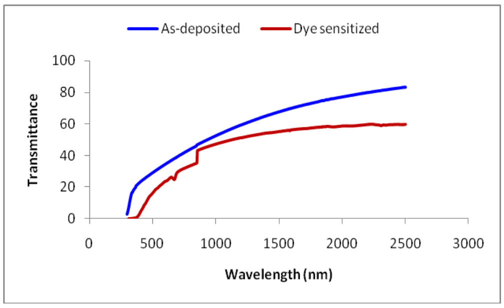


Fig. 4. Transmittance spectra of as-deposited and dye sensitized $TiO_2$ thin film

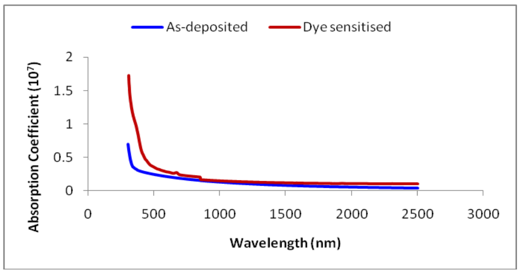


Fig. 5. Variation of absorption coefficient of dye sensitized $TiO_2$ thin film with wavelength.

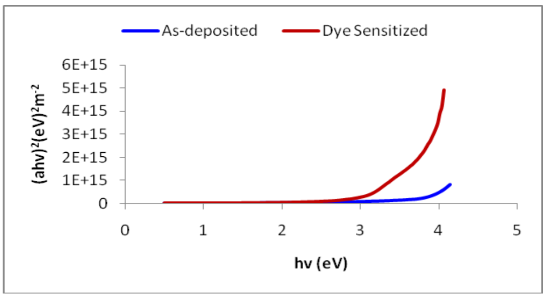


Fig. 6. $(\alpha h\nu)^2$ vs. hν plot of dye sensitized $TiO_2$ thin film.

where $K$ is a constant, hν is photon energy, $E_g$ is the optical band gap and 'n' is a constant equal to 1 for direct band gap and 4 for indirect transitions. $(ahv)^2$ vs. $hv$ plot of as-deposited and dye sensitized $TiO_2$ thin film is shown in Fig. 6. The direct and indirect band gap values obtained for as-deposited thin and annealed film samples are given in table II. The direct band gaps of the films initially increases with growth rate and then decreases. The indirect band gap of the films initially decreases with growth rate and then increases. Minimum value of direct band gap is obtained for the films deposited at higher growth rate and this may be due to the higher thickness of the films. Accordingly, the indirect band gap of the films deposited at lower growth rate had maximum value.

TABLE II: EFFECT OF DYE SENSITIZATION ON OPTICAL BAND GAP OF AS-DEPOSITED $TiO_2$ THIN FILM.

| Sample | Growth rate (nm/cycle) | Band gap (eV) | | | |
|---|---|---|---|---|---|
| | | As-deposited | | Dye sensitized | |
| | | DIRECT | INDIRECT | DIRECT | INDIRECT |
| Sample 1 | 6.89 | 3.80 | 3.0 | 2.8 | 2.9 |
| Sample 2 | 7.02 | 3.95 | 2.1 | 3.2 | 2.0 |
| Sample 3 | 10.40 | 3.50 | 2.2 | 3.7 | 2.9 |

The samples deposited at different growth rates are sensitized by the natural dye obtained for Clitoria Ternatea. The effect of dye sensitization on the optical band gap of as-deposited $TiO_2$ films are shown in table III. The dye sensitization of the film is found to have profound effect in the optical properties of the films. The remarkable observations are given below.

- Optical transmittance of the film decreased by a larger magnitude upon dye sensitization(Fig. 4)
- Absorption Coefficient of the films is increased by an order of $10^1$ (Fig. 5)
- The direct and indirect optical band gap of the film decreased upon dye sensitization (Table II)

  These results show that the $TiO_2$ thin films sensitized with the natural dye extracted from *Clitoria Ternatea* can be employed as efficient absorber in DSSC.

## IV. CONCLUSION

$TiO_2$ thin films are deposited by SILAR method. Post deposition annealing of the films improved the crystallinity of the films. Direct and indirect band gap of the $TiO_2$ thin films deposited at different growth rate is in the range of 3.5-3.9 and 2.1-3.0 eV respectively. The effect of dye sensitization on the optical properties of the film is analysed. Dye sensitization improved the optical absorption of the films and a red shift in the optical band gap of the film is observed upon dye sensitization.

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