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Synthesis and characterization of undoped and sliver doped titanium dioxide thin film by using sol-gel spin coating method

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***Abstract*—In this paper, structural and optical properties of undoped and sliver doped titanium dioxide film have been studied. By using Sol-gel method undoped and sliver doped titanium dioxide (TiO_2) thin film synthesis on FTO glass substrate. Sliver has been doped 3%,7%, concentration in titanium dioxide (TiO_2) .Different properties such as, crystal structure, phase identification, thickness, band gap, transmission and absorption spectrum have been studied using X-ray diffraction (XRD), Raman spectroscopy, UV/Vis spectrophotometry. The results showed that undoped and Ag doped TiO_2 thin film annealed at 450^{o}c had anatase phases and there is no Ag peaks in X-ray diffraction.**

Keywords— Titanium dioxide, sliver, sol-gel spin coating, structural properties

I. Introduction

Titanium oxide is a semiconductor material having wide range of implementation in photo catalysis, corrosion protective coating, self-cleaning devices, gas sensor, energy storage and optical [1]. All these applications are based on morphology, crystallographic structure and physical properties of different phase of titanium. TiO_2 can show three forms brookite, rutile and anatase as a bulk material while thin film of TiO_2 can exhibit only rutile, anatase and amorphous. By using chemical deposition techniques brookite film can obtained using annealing temperature. Rutile is most stable phase and anatase and brookite can be transferred into rutile by annealing at high temperature [2-4]. Titanium dioxide has a band gap of 3.2ev, 3.0ev, 1.9ev for anatase, rutile and brookite respectively.

Titanium oxide is non toxic and chemically stable having electrochemical, exceptional physical, photoactive and electronic properties [5-8]. Due to its commercial and technological potential, much work has doing on this material [9, 10]. Titanium oxide involve in many applications such as water purification, lithium batteries, dielectric layer, gas sensing, solar cell, resistive switching etc [11-17]. Different method was adopted to increase their efficiency and applicability. By doping rear earth and transition metal in TiO_2 thin film provides different changes in its structural and optical properties which is very beneficial for different applications. Silver is among most studied metal as dopant in TiO_2 [18]. It gives better result and efficiency especially in antibacterial properties [19].

Because of this reason, numerous scientists have researched on the growth of thin films of TiO_2 on the multiple substrates i.e. polycarbonate, glasses and copper by using different techniques such as vapor deposition, thermal oxidation and magnetron sputtering [20-22]. Table 1 is explaining the comparison of Ag doped TiO_2 materials [23-28]. In literature very little work is available on the Ag doped TiO_2 specifically on the FTO template using the spin coating technique. In our study FTO templates were used and undoped, 3% and 7% sliver doped TiO_2 films were synthesized by sol-gel spin coating method. optical and structural properties of undoped and sliver doped TiO_2 were studied in detail.

II. Experimental Method

A. *Preparation of solutions*

0.12 mole solutions was prepared. Silver nitrate ($AgNO_3$) and titanium isopropoxide ($C_{12}H_{20}O_4Ti$) precursors were used as initial materials to synthesize the undoped and sliver doped solutions. Specific molar ratios of precursors are measured for all Titanium based solutions. Firstly, 0.4 ml of titanium isopropoxide was hydrolyzed in 10 ml ethanol under the magnetic stirring for 20 min under room temperature to get undoped solution. After that 1ml acetic acid was added in the solution and again stirred for 30 min at magnetic stirrer. For making the doped solution of Ag in TiO_2, Sliver nitrate ($AgNO_3$) was used as additional precursor in simple TiO_2 solution. 3% and 7% weighted used for doping and 6.98mg and 16.29mg sliver nitrate precursor used respectively. Sliver doped solution TiO_2 solution stirrer for 4 hours at magnetic stirrer at room temperature.

B. *Deposition of TiO_2 based films on substrates*

Different methods are available for thin film formation but the most simple and less expensive method which used for deposition of solution of silver doped and undoped on FTO template was sol-gel spin coating method. Before the deposition, substrate cleaning process was done. The FTO template was cleaned by an ultrasonic bath in acetone, poly ethylene glycol, ethanol and deionized water respectively,

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for each 15 min. Drying process was done in air to remove any surface contamination. . After completing the cleaning process, Solution is spin coated at 3000 rpm for 30sec. After the deposition thin film is dried at 100°C for 10 min. This cycle is repeated for 5 times. Annealing was done at 450°c for 30 min in air for good uniform films. Film thickness about100 nm in both undoped and sliver doped TiO_2 films measured from Ellipsometry. Complete process explains in figure 1.

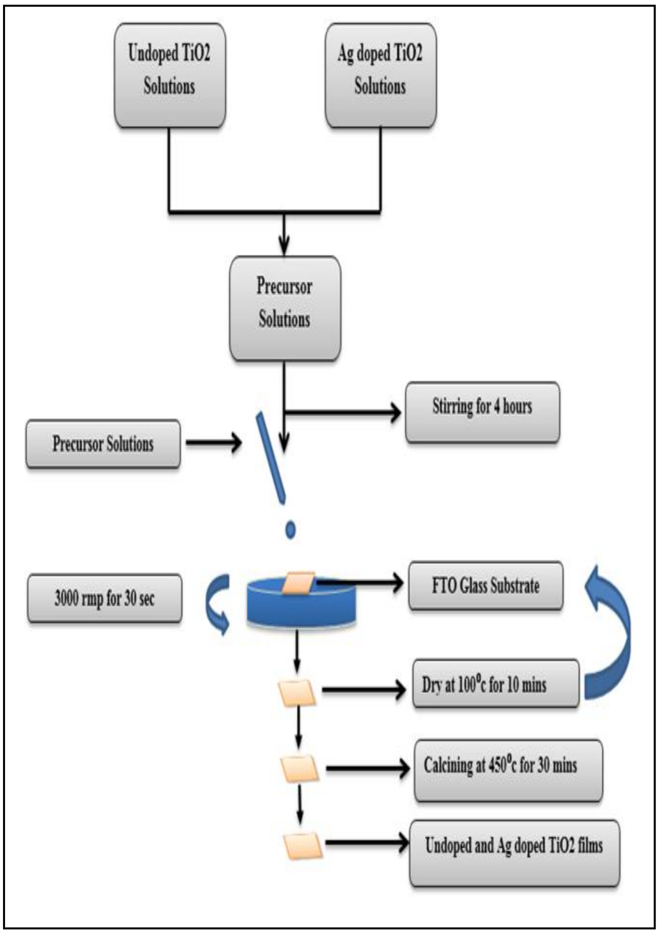

Fig.1.flow chart of spin coating method of undoped and sliver doped TiO_2 films.

III. Results and discussion

A. *XRD Studies*

The crystal structure was examined by using X-Ray Diffraction. Figure 2 shows the patterns of undoped and Sliver Doped TiO_2 using XRD. The TiO_2 thin film that was synthesized by the sol-gel spin coating method showed the sharp and intense diffraction peaks at 25.40(101), 48.15(200), 54.67(211), 61.63(204) match with the JCPDS values (pdf card no: 00-021-1272) which correspond to anatase phase. . It is clear from XRD patterns that there are no characteristic peaks related to sliver or its oxides of Ag doped films. By increasing Sliver content intensities of peaks decreases and there is slight shift in peaks due to doping. It is reported that sliver doping improves the crystallization of Titanium dioxide in some cases, while decrease or remain same in other cases [29] . So, it can be examined that the intensities of film peaks showed very little decreasing tendency with increasing the Ag content. Instead of fact that there is a big variation between ionic radius of Ti^{4+}(74.5 pm) and Ag^{+}(129pm) the existence of Ag content did not cause major varieties in crystallization. * represents the peaks of FTO Template.

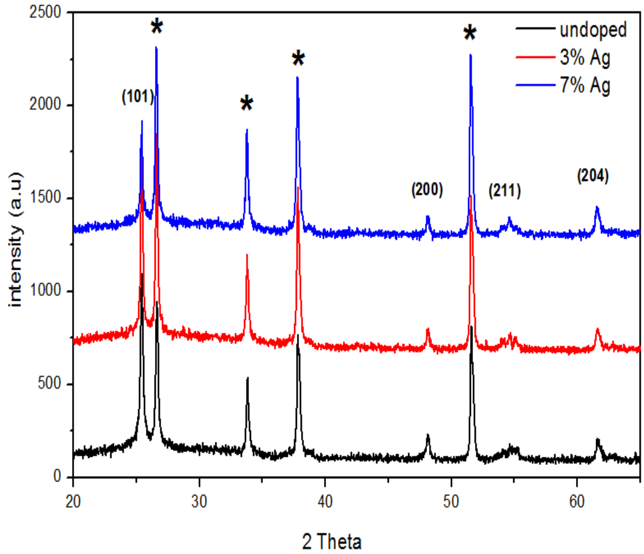

Fig.2. XRD patterns of TiO_2 based films.

B. *Raman Spectroscopy*

To further clarify the structural study of undoped and Ag-doped TiO_2 obtain in XRD, Raman measurement were done at room temperature. Figure 3 displays Raman spectra of undoped and silver doped TiO_2. Typically, Titanium dioxide anatase phase has four Raman vibrational phonon modes, named as E_g, A_{1g}, B_{1g} modes [30]. Figure 3 clearly shows all four Raman vibrational phonon modes of Anatase phase at 148 , 390, 510 , 632. There is no peak regarding to sliver or its oxides seen in Raman spectra. By increasing Sliver content Raman peaks width increases while intensity decreases which indicating degradation of crystalline quality of titanium dioxide thin film due to large size of Ag^{+} ions.

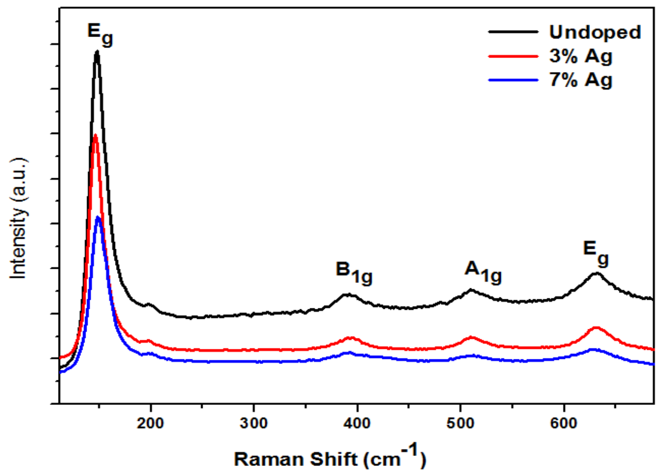

Fig.3. Raman spectra of TiO_2 films.

C. *Spectrophotometric studies*

The undoped and sliver doped TiO_2 films were analyzed by UV-visspectroscopy. Figure 4 shows optical transmission spectra of the undoped and Sliver doped Titanium dioxide thin films in the visible region. Undoped TiO_2 film is transmission is ~35% and with the addition of Ag in TiO_2 film transmission decreases due to structural defect created in the lattice. Overall low transmission rate is due to large thickness of films.

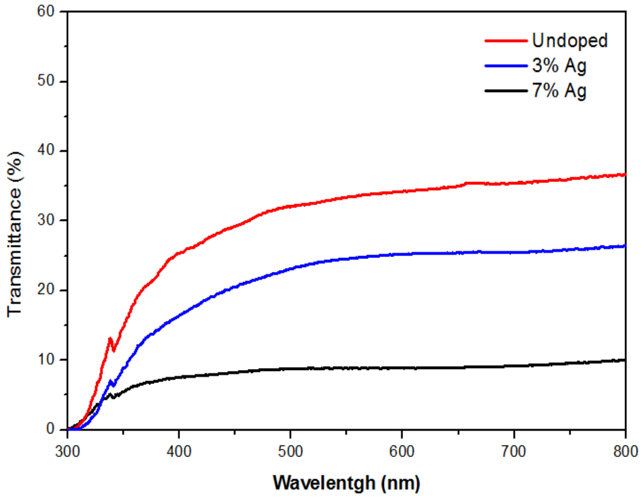

Fig.4. Transmission spectra of undoped and sliver doped TiO_2 films.

Figure 5 shows the absorbance of undoped and sliver doped TiO_2 films. Absorbance of both undoped and sliver doped TiO_2 films sharp decrease in visible region (>350nm) . Doped films have smaller absorbance as compared to undoped film. Ag doping can have influence on absorption of light. Doping of Ag can have significantly influence on the absorption of light. By increasing doping amount, it is clear that in absorption spectra absorption edge shift.

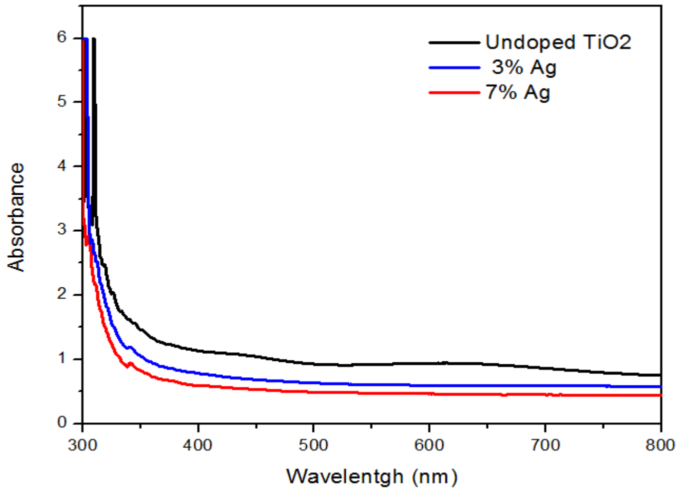

Fig.5. Absorbance spectra of undoped and sliver doped TiO_2 films.

The band gap energy of undoped and sliver doped TiO_2 thin films was calculated by using Tauc's relation for direct band gap material from transmission spectra.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

The absorption coefficient value was calculated using the relation

$$\alpha = \frac{-\ln T}{t} \text{ nm}^{-1} \quad (2)$$

Here t represents thickness and T represent transmission spectra.

Table 1:
Band gap energy values of undoped and sliver doped TiO_2 films.

Film	E_g (eV)
undoped	3.35 eV
3% Ag	3.31 eV
7% Ag	3.26 eV

Band gap of undoped TiO_2 is 3.35 eV and sliver doped TiO_2 films band gap energy of 3.33 eV and 3.27 eV for 3% and 7% sliver doping concentration respectively. Table 1 shows band gap of all films. Defective energy levels formed below conduction band are responsible of low band gap in sliver doped TiO_2 and these defective energy levels formed due to structural defects. Since the structural defects are related to Ag concentration so band gap energy decreases slowly with the increasing of Ag concentration in Titanium dioxide thin films.

IV. Conclusion

In this study, undoped and sliver doped TiO_2 thin film prepared by low cost and simple sol-gel spin coating method. Structural properties were studies by XRD, Raman spectroscopy and optical properties studies using spectrophotometry. XRD and Raman shows that both undoped and sliver doped films in anatase phase with good crystalline structure. By increasing sliver content crystal quality decreases. The method used in this study is to provide a low cost, low temperature and simple synthesis of titanium dioxide thin film with good properties TiO_2 thin film has large area of application from resistive switching to photo catalysis and sliver doped TiO_2 also large area of applications.

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