Structural and optical properties of silver doped TiO₂ thin films for solar cell applications

V.V.S. Murty and Vinay Dashore
Physics Department, Govt. Autonomous Holkar Science College, Indore-452017, India

e-mail: drvvsmurty@yahoo.co.uk

Abstract. Electron collection efficiency and hence the device performance of a dye sensitized solar cell can be increased by localized surface plasmons (LSP) produced by the thin films of 2% silver doped TiO₂ photo electrode. These films of silver doped TiO₂ on glass substrates are prepared by pulsed laser deposition (PLD) method and have a lowest grain size of 8-31 nm. XRD, AFM and raman studies are made to characterize the surface at various annealing temperatures and annealing time durations. The lowest grain size of 8 nm of these films developed.

1. Introduction
The widespread use of solar photovoltaic technology for terrestrial and domestic applications is limited due to its high cost per unit watt. Thin film and hence nano film based solar cell is one of the best options. Nano particles (Ag or Au, with particles sizes in the range of 8 to 100 nm) are deposited on the solar cell surface, due to surface plasmon resonance excites and enhances the electromagnetic field near the metal surface where the absorption of photon increases[1]. The maximum absorption wavelength of plasmonic particles has been found to dependent on factors such as size, shape, and dielectric environment [2]. This property is exploited in photo voltaic cell to improve photo current through its spectral response. Silver doped composite thin films show that they are nano crystalline in nature, highly transparent, homogeneous with no visible pinholes and suitable for solar cell applications [3]. In the present study, silver doped TiO₂ thin films are prepared by Pulsed Laser Deposition (PLD) method on glass substrate. Dependence of various parameters is studied at different annealing temperatures suitable for solar cell applications.

2. Experimental
In our experiment thin films are prepared by PLD method. It has four different stages. It include the ablation process of the target material by the laser irradiation, the development of a plasma plume with high energetic ions, electron as well as neutrals and the crystalline growth of the fim itself [4-5]on the heated substrate.

TiO₂ Powder (Molecular Weight 79.9, Purity 99.9%) was mixed with Ag₂O(Molecular Weight 231.749, Purity 98.9%) and ground for 6 hours by wet ball mixing using acetone/alcohol as solvent and pressed to target at hand pressure. The target having dimensions of thickness 2mm and diameter 24mm were prepared after sintering 1200° C for 8 hours. Target was mounted on pellet with silver epoxy by heating for 2 hours. Target along with pellet was fixed in PLD chamber. Si substrate was arranged on sample holder in PLD chamber. Film of TiO₂ mixed with Ag₂O was deposited by using
rotating arrangements in PLD chamber by PLD technique. The base pressure was bought down to $3 \times 10^{-6}$ torr and thin film a deposited at a working pressure of $1 \times 10^{-4}$ in an ultra pure oxygen atmosphere. The target was ablated with KrF exclaimer laser pulse (248 nm) that was synchronized with rotational motion. Films deposited under laser power of 230 mJ with repetition rate of 10 Hz and duration of 10 minutes. During the deposition, the distance between target and substrate is maintained at 5 cm. Post annealing was performed in oxygen atmosphere at 435°C for 105 minutes with pressure of $1 \times 10^{-4}$. Substrate was cooled for 90 minutes gradually by decreasing the temperature in presence of oxygen atmosphere by reducing the heater current of 0.5 ampere step by step interval of 10 minutes.

3. Results and discussion
To evaluate the performance of plasmon resonance effect and to enhance the efficiency of photochemical cells, thin films of TiO$_2$ is doped with 2% Ag (By molecular weight) particles on glass. We found that the photo response in the visible region is increased. These results suggest that plasmon resonance effect contributes to the enhancement of photocurrent, and indicates the possibility of improving the energy conversion efficiency with silver doping. The characterization of the film is to study 1. surface morphology 2. optical Properties.

3.1 XRD analysis
The XRD peaks slightly different in silicon substrate is shown in fig 1. These differences can be attributed to the differences in particle size between the samples. In order to quantify the particle size effects, we can estimate the mean grain size ($L$) of these samples by applying the scherrer equation

$$\beta(2\theta) = \frac{K\lambda}{L\cos\theta}$$

where $K=0.94$ Constant and $\beta(2\theta)$ Full width half maximum $L$= grain size, and $\lambda$ is the wavelength of X-rays, $\beta(2\theta)$ is the pure full width of the diffraction line at half the maximum intensity, and $\theta$ is the bragg’s angle.

![Figure 1. XRD pattern of the Ag covered TiO$_2$ on glass substrate with annihilated with different temperture A (496°C) b B(435°C)](image)
Table 1: XRD Data of silver doped thin films at various substrate temperatures

| Sample       | 2θ     | Grain size |
|--------------|--------|------------|
| Glass 435°C  | 51.1695| 18nm       |
| Glass 496°C  | 30.9354| 8 nm       |

The mean grain sizes of samples A and B are 18 and 8 nm, respectively.

3.2 AFM Analysis

Figure 2 shows the AFM images of the samples obtained after heating at 435°C and 496°C. It is obvious from these images that these samples of Ag covered TiO₂ particles are disperse, with an average particle size of 25 nm-35 nm for sample A and 5 nm-21 nm for sample B. The particle size of samples A and B are determined from the AFM images are in good agreement with the values determined from the XRD analysis. XRD and TEM results (table 1 and 2) show that the size-selected Ag covered TiO₂ nanoparticles were prepared from the SSR method and that both samples A and B have an anatase structure.

![AFM images](image_url)

Figure 2 Ag covered TiO₂ on glass substrate (a) 435°C (500nm×500nm) sample A and (b) 496°C (976.6nm×976.6nm) sample B

Table 2: AFM results of Ag covered TiO₂ on glass substrate 435°C and Ag covered TiO₂ on glass substrate 496°C

| S.No | Sample       | Hole   | Hill   | Intervals |
|------|--------------|--------|--------|-----------|
| 1    | Glass 435°C(A)| 29.01% | 70.97% | 70.96%    |
| 2    | Glass 496°C(B)| 42.33% | 57.69% | 57.53%    |

3.3 Raman Analysis

The ultimate goal in light-harvesting technologies such as solar cells is to collect as much sunlight as possible and to efficiently convert this light into useful electricity. As the presence of non-crystalline silicon leads to reduced conversion efficiency, Raman spectroscopy is one such tool that is widely used in the solar industry to monitor the highly crystalline, defect-free and strain-free silicon films/layers.

The ability to quantify both thermal and interfacial stress in solar cell materials is critical. Stress can dramatically impact conversion efficiencies in PV cells. It is critical to understand the location of the stress and their impact on the cell performance and improvement for process yields [7].

Raman spectroscopy provides a direct measurement of stress (or strain) in silicon based solar cells by monitoring the spectral position of the 520 cm⁻¹ peak on the sample, from which a stress map can be
generated with sub-micrometer spatial resolution. As result, Raman spectroscopy provides direct insight into solar cell processing and prevents less efficient cells from leaving production. High-performance Raman spectroscopy using filters with steep edges and small transition widths allows one to detect low-energy vibration modes. From fig. 3 Raman peak at 558.06 cm$^{-1}$ for the sample annealed at 496°C (1) and Raman peak at 557.014 cm$^{-1}$ for the sample at 435°C (2).

![Graph](image)

Figure 3. 2% silver doped TiO$_2$ films at 496°C (1) and 435°C (2) on glass substrate exhibit green photonics for PV Technology detect low-energy vibration modes

4. Conclusion
Understanding the temperature dependent behaviour of Ag covered TiO$_2$ on glass substrate, for calculating grain size and porosity is key behaviour for exhibiting the various properties of a solar active device. In this study, it is observed that particle size and porosity depends on temperature. The size and structure of 2% Ag covered TiO$_2$ on glass nano particles are calculated by using XRD,AFM. The XRD patterns and AFM images showed that the prepared samples of 2% Ag covered TiO$_2$ on glass substrate produces nano particles with an average particle size of 18 nm-35 nm (sample A), and 5 nm-21 nm(sample B). The raman spectra revealed that samples A and B have detected low-energy vibration modes of green photonics useful for PV technology.

Acknowledgement
The authors are very grateful to Ajay Gupta, Ram Janay Choudhary, V. Ganeshan, Mukul Gupta and Vasanth Sathe UGC –DAE-CSR, Indore, India. The authors are also very much thankful to R.K. Tugnawat, Govt. Autonomous Model Holkar science college, Indore, India.

References
[1] Schaad D M, Feng B and Yub E T 2005 Appl. Phys. Lett. 86 063106 .
[2] Kelly K L, Coronado E, Zhao Lin Lin, and Schatz George C. 2003 J. Phys. Chem. B 107 668.
[3] Saikia D., Saikia P. K., Gogoi P. K., Saikia P. 2011 Digest Journal of Nanomaterials and Biostructures 6 589.
[4] Handbook of Analytical Methods for Materials 2001 (Materials Evaluation and Engineering Inc.) p.7-10.
[5] Shaw D. G. and Langlois M. C 1993 Proc. Soc. Vac. Coaters 36 348.
[6] Schrader B. (Ed.) 1995 Infrared and Raman Spectroscopy: Methods and Applications (Chichester: John Wiley)
[7] Grasselli, J. G., Bulkin, B. J. (Eds.) 1991 Analytical Raman Spectroscopy; (Chichester: John Wiley)