Growth of Silver Nanoparticles on Titanium Dioxides Layer for Plasmonic-Based Solid-State Solar Cells

Sanjay K Sardana[*1, 3], Piyush K Parashar[2], P S Chandrashekar[2], Sanjay K Srivastava[3] and Vamsi K Komarala[2]

[1]*Department of Physics, Government National College Sirsa, Haryana, India*
[2]*Centre for Energy Studies, Indian Institute of Technology Delhi, New Delhi, India*
[3]*Inorganic PV Devices Group, CSIR-National Physical Laboratory, New Delhi, India*

*Email:sanjay84sardana@gmail.com

Abstract. In this work, we presented a simple method for the growth of silver nanoparticles (Ag NPs) which forms spontaneously during the RF sputtering onto titanium dioxides (TiO_2) layer, prepared by spray pyrolysis. The formation of Ag NPs is achieved due to the rough nature of the TiO_2 layer. As, TiO_2 is a wide band gap semiconductor material, which would only absorb the UV part of the solar spectrum. The photovoltaic activity of TiO_2 based solid state photovoltaic system can be further improved using metallic nanostructures. The Ag NPs forms a Schottky barrier solar cell with the TiO_2 layer. Upon illumination, hot electrons from Ag NPs gets injected into the TiO_2 layer which leads to charge separation. Here, Ag NPs works as absorbing material in the visible region, are capable of increasing the absorption of TiO_2 and hence the performance of plasmonic-based solid-state TiO_2/Ag solar cells.

INTRODUCTION

Plasmonics is a branch of photonics/nanophotonics which deals with the interaction of light with metal nanostructures. In the past few years, the field of plasmonics has emerged as a rapidly expanding new area for materials and device research. Plasmonics open the possibility to amplify, concentrate and manipulate light at the nanoscale, and allows overcoming the diffraction limit of traditional optics, and consequently, concepts can be adopted in a wide range of applications varies from biosensing to photovoltaics [1,2]. Plasmonics provides a novel approach for achieving the light trapping in solar cells by the use of metallic nanostructures that support localized surface plasmon resonances: excitation of conduction electrons at the interface between the metal and dielectric. With proper design and engineering of these metallo-dielectric structures light can be concentrated and folded into a thin semiconductor layer, thereby increasing the absorption process. Consequently, these metal nanostructures can be integrated into photovoltaics as efficient light trapping scheme to increase the efficiency of conventional devices. However recent investigations have shown that plasmonic nanostructures can also directly convert the collected light into electrical energy by generating "hot electrons"[3-5]. After light absorption in the nanostructures which lead to surface plasmon excitations, plasmons can decay to the ground state by transferring its accumulated energy to conduction electrons of the metal nanoparticles. This process produces high energy electrons, also known as "hot electrons", which have sufficient energy to overcome the potential barriers provided by a thin layer of semiconductors when the plasmonic nanostructures in contact with a semiconductor, thereby forming a metal-semiconductor Schottky junction. This new scheme for solar energy conversion opens up a way to realize new photovoltaic devices.

In this study, we optimized the TiO_2 layer, prepared by the spray pyrolysis for spontaneously growth of silver nanoparticles during RF magnetron sputtering.

DAE Solid State Physics Symposium 2018
AIP Conf. Proc. 2115, 030626-1–030626-4; https://doi.org/10.1063/1.5113465
Published by AIP Publishing. 978-0-7354-1851-6/$30.00

EXPERIMENTAL DETAILS

Fluorine-doped tin oxide (FTO) glass substrates were cleaned with soap solution, deionized water, acetone, and isopropyl alcohol by ultrasonication for 30 minutes each. The TiO_2 layer was deposited on cleaned FTO glass substrates by employing spray deposition method. Prior to the deposition, substrates were heated to 450°C and after deposition, heating was continued for 15 min. (TiO_2 precursor solution was prepared by adding titanium di-isoprpoxide bis-actylacetone to anhydrous ethanol in 1:9 volume ratio).The silver nanostructured thin films on aTiO_2 thin layer deposited FTO glass substrates were prepared by RF magnetron sputtering method. Magnetron sputtering system has the option for large area uniform deposition with 2" x 6" rectangular silver target (99.99% pure) as the cathode. The distance between the cathode and substrate is around 10 cm. Initially, the sputter chamber was evacuated to a base pressure of 2 x 10^{-6} mbar and then deposition was carried out onto TiO_2 thin layer deposited FTO glass substrates for 60 second at a constant working pressure of 2 x 10^{-2} mbar in argon gas environment (gas flow rate = 15 sccm) with the RF power of 20 W. The surface morphology of TiO_2 layer and Ag NPs integrated TiO_2 layer have been studied by Scanning electron microscope (SEM) and Atomic force microscope (AFM). The optical properties of the TiO_2 layer were carried out with the help of PerkinElmer Lambda 1050 double beam UV-Vis-NIR spectrophotometer.

RESULTS AND DISCUSSION

Fig. 1(a) shows the schematic of solar cell structure, where front contact has been taken from FTO glass and Ag serves as back contact as well. Fig. 1(b) shows the transmittance spectra of TiO_2 layer of different thickness deposited on FTO coated glass. It is to be noted that transmittance measurement of the TiO_2 layer is normalized to FTO coated glass substrate. The average transmittance of the TiO_2 layers is above 80% in the visible region. We have also calculated the thickness of TiO_2 films from these transmittance spectra by usingenvelope method. The refractive index n of the TiO_2 film at different wavelength is calculated from the transmission curve as given below

$$n = \left[N + (N^2 - n_s^2)^{\frac{1}{2}} \right]^{\frac{1}{2}}$$

where

$$N = \frac{2n_s(T_M - T_m)}{T_M T_m} + \frac{n_s^2 + 1}{2}$$

and n_s is the refractive index of the substrate. Here,$n_s = 1.90$
Using these equations we calculated the thickness, t as

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}$$

Where n_1 and n_2 are refractive indices at the given value of λ_1 and λ_2.

Sample No.	Thickness (nm)	Bandgap (eV)	Mean-transmission ($350nm - 800\ nm$)
1	1253	3.67	83.35
2	1185	3.67	83.30
3	1509	3.69	82.22

Fig. 1(c) shows the plot of $(\alpha h\nu)^2$ vs $h\nu$, where α is the absorption coefficient defined as $\alpha = (1/t) \log(1/T)$and hν is the energy of the incident photon. Further we have calculated the band gap of the TiO_2thin films. The energy gap (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression:

$$\alpha h\nu = K(h\nu - E_g)^{\frac{1}{2}}$$

where K is a constant, E_g is determined by extrapolating the straight line portion of the spectrum to $\alpha h\nu = 0$. From the calculation the optical band gap of TiO_2 layer is found to be ~3.67eV

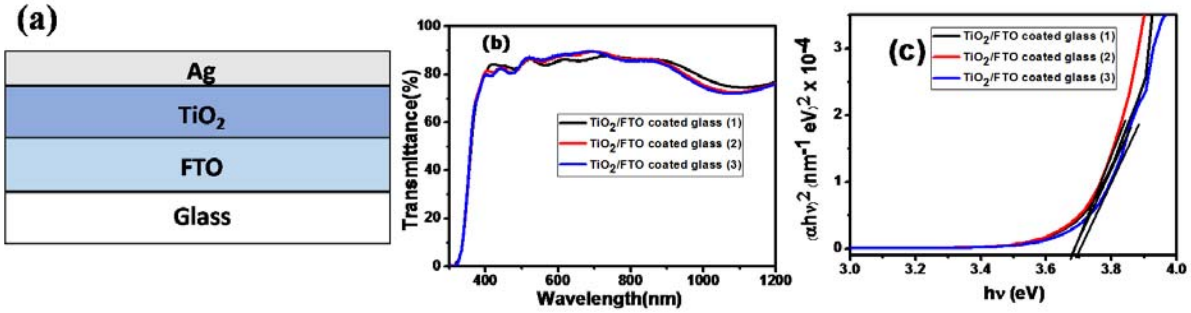

Fig. 1(a) schematic of solar cell structure, 1(b) transmittance spectra of TiO_2 layer of different thickness, and 1(c) corresponding plot of $(\alpha h\nu)^2$ vs hν.

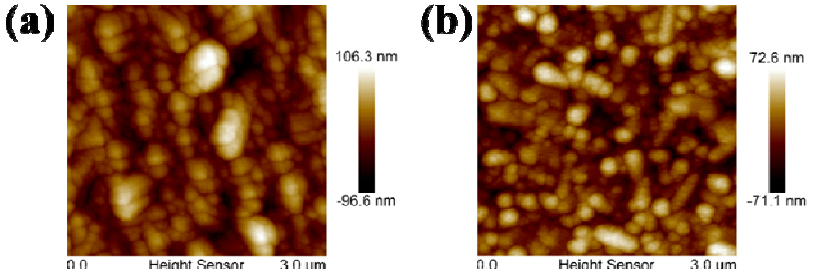

Fig. 2 AFM images of (a) bare FTO coated glass substrates, (b) TiO_2 layer deposited FTO coated glass substrates.

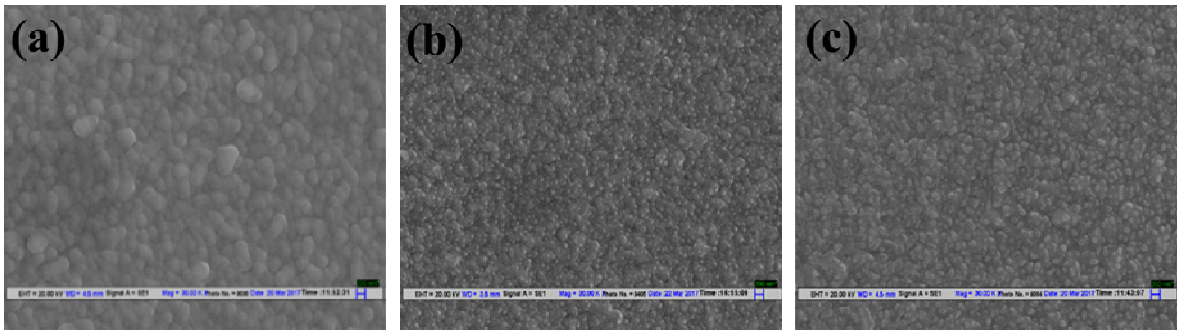

Fig. 3 SEM images of(a) bare TiO_2 layer on FTO coated glass, (b) TiO_2 layer with Ag NPs for 40s deposition, and (c) TiO_2layer with Ag NPs for 60s deposition.

Fig. 2 shows the AFM images of (a) bare FTO coated glass substrates, and (b) TiO_2 layer deposited FTO coated glass substrates. We have optimized the thickness of the TiO_2 layer to get the required surface roughness of the film for the spontaneous formation of Ag NPs during sputtering itself. Fig. 3 shows the SEM images of (a) bare TiO_2 layer on FTO coated glass, (b) TiO_2 layer with Ag NPs for 40s deposition, and (c) TiO_2 layer with Ag NPs for 60s deposition. From fig. 3 (b), it is clear that we got Ag NPs on TiO_2 surface, which is inhomogenous in size and shape and also do not cover the TiO_2 surface completely. The TiO_2 surface roughness and structuring is the responsible for formation of Ag NPs. With further increase in the sputtering time of Ag, the Ag NPs size and surface coverage on the TiO_2 surfaceincreases see fig. 3 (c). H. N. Barad *et al.,* shown that increase in the photocurrents with increase in the Ag thickness lead to higher amount of absorbing material i.e., Ag NPs. Hence there is large amount of SPR excitation leading to more "hot electrons" to be generated and injected into the TiO_2 layer. They have achieved short circuit currents of 1.18mA/cm^2, and open circuit voltage of ~380mV and conversion efficiency of 0.2% which is highest efficiency that has been achieved for a solid state TiO_2/Ag Schottky barrier hot electron plasmonic solar cell. However, in our case we obtained short circuit current of 480μA/cm^{2}and open circuit voltage of 78.4 mV only. So, we still required further optimization of TiO_2 layer thickness and its surface roughness as well as Ag NPs distribution on TiO_2 surface to have maximum hot electron capture into the TiO_2 layer.

CONCLUSION

In this work, we demonstrated a simple method to form Schottky junction based TiO_2/Ag plasmonic solar cells. The silver was deposited by sputtering onto a rough TiO_2 surface which was deposited by spray pyrolysis method. The surface roughness of TiO_2 layer is very critical for the formation of Ag NPs during sputtering itself. Here, Ag not only play the role of absorbing material for generating "hot electron" but also serves as the back contact for charge separation.

ACKNOWLEDGEMENTS

One of the author's Dr. Sanjay K Sardana would like thanks the fellowship reference no. PDF/2016/002557 from SERB, a statutory body of the Department of Science and Technology, Government of India. Authors would like to acknowledge the Nanoscale Research Facility and Central Research Facility of IIT Delhi for the structural and optical characterization of samples.

REFERENCES

1. S. A. Maier, Plasmonics–Fundamentals and Applications (**Springer: New York, 2007**)
2. A Polman and H. A. Atwater,"Plasmonics for improved photovoltaic devices" *Nature Materials***11(2012)174**
3. C Clavero,"Plasmon-induced hot electron generation at nanoparticle/metal oxide interfaces for photovoltaic and photocatalytic devices", *Nature Photonics***8 (2014) 95**
4. M. L. Brongersma, N. J. Halas and P. Nordlander,"Plasmon-induced hot carrier Science and Technology", *Nature Nanotechnology***10 (2015) 25**
5. H.N. Barad, A. Ginsburg, H. Cohen, K. J. Riewyk, D. A. Keller, S. Tirosh, Y. Bouhadana, A. Y. Anderson, and A. Zaban,"Hot electron based solid state TiO_2/Ag solar cells", *Advanced Material Interfaces***3 (2016) 1500789**