Proceedings of the Technical Sessions, 24 (2008) 44-50
Institute of Physics – Sri Lanka

Study of charge transport and carrier lifetime in dye-sensitized solar cells made from gold particle embedded SnO_2 films

R. Chinthaka L De Silva, L. S. G. Liyanage and V. P. Susira Perera*
Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda

ABSTRACT

The performance of dye-sensitized solar cells made from SnO_2 improved by embedding gold nano-particles in the mesoporous SnO_2 films. Both the photocurrent and photovoltage of these cells increased by incorporating gold nano-particles. This enhancement was studied by measuring the diffusion coefficient and lifetime of charge carriers in SnO_2 films. It was observed that the diffusion coefficient and lifetime of charge carriers in gold particle embedded SnO_2 films are greater than bare SnO_2 films. The films with higher diffusion coefficient is attributed to long-distance traverse of charge carriers in the film while long lifetime indicates low recombination rate.

1. INTRODUCTION

Dye-sensitized solar cells (DSSC) based on nanoporous films of metal oxides have gained much attention as alternative to the silicon solar cells because of their prospect for low cost photovoltaic energy conversion. In this context promising solar to electrical energy conversion efficiencies of more than 10% have been achieved for DSSC based on TiO_2 [1]. However the efficiency of DSSC constructed with other candidates of metal oxides such as ZnO, Nb_2O_5, SnO_2 etc., lies much more behind [2]. SnO_2 is an attractive semiconductor material for DSSC as well as for other optoelectronic devices because of its high photo stability and good carrier mobility. SnO_2 is high band gap semiconductor as TiO_2 and ZnO, but the conduction band edge of SnO_2 is located at a lower level in the energy scale [3]. Due to this reason one would expect a low open circuit photo voltage for DSSC constructed with SnO_2. Therefore selecting SnO_2 as the semiconductor material of DSSC even a small development in the photo voltage, which become marginal for TiO_2 or ZnO, can be clearly noticed.

In this article we report our results of construction of a dye-sensitized solar cell with composite made combining SnO_2 with gold nano-particles. Here the efficiency of the solar cell is enhanced by increasing both the photocurrent and the photovoltage. Our results clearly indicate that the diffusion coefficient and lifetime of charge carriers increased by incorporating gold nano particles to the SnO_2 films.

2. EXPERIMENTAL

In the preparation of the SnO_2 films, 1 ml of SnO_2 colloidal solution (Alfa chemicals), a few drops of glacial acetic acid and a sufficient amount of ethanol were added together in an agate mortar and mixed well. A known volume of gold chloride hydrate ($AuCl_4H$) from $3x10^{-5}$ M solution was added to the above mixture in the preparation of gold particle embedded SnO_2 films. Then the solution was transferred to a beaker and sonicated after addition of 30 ml of ethanol. This solution was sprayed onto 0.5x 1.0 cm^2 conducting tin oxide (CTO) glass plates and sintered at 550 °C in a furnace. These electrodes were dipped in a solution of Indoline dye dissolved in ethanol for about one and half hours to get the dye coated. Photoelectrochemical cells (PECs) were fabricated by clamping a Pt sputtered CTO glass plate onto the dyed surface and filling the capillary space with the electrolyte (0.5M 4-tert-butylpyridine, 0.5M tetrapropylammonium iodide, 0.1M iodine, in 4:1 ratio mixture of ethylene carbonate and acetonitrile). I-V characteristics of the cells were recorded using a Keithley 2420-3A source meter and a 1.5 AM, 1000 Wm^{-2} solar simulator lamp. The intensity modulated photocurrent spectroscopy (IMPS) and intensity modulate photovoltage spectroscopy (IMVS) were also measured using a blue light emitting diode (LED) of wavelength, λ = 470 nm as the light source driven by a frequency response analyzer with a DC bias. LED provides both the AC and DC components of the illumination.

3. RESULTS

We have prepared quantum size particles of gold on SnO_2 colloids of ~20 nm and those SnO_2 colloid which we refer as Au/SnO_2 here after was used to fabricate films of dye-sensitized solar cells. It is not difficult to observe gold nanoparticles embedded in SnO_2 film with a SEM picture (figure 1). The average particle size of SnO_2 in the film is around 100 nm. The performance of the dye-sensitized solar cells constructed with above films was compared with bare SnO_2 films in this study.

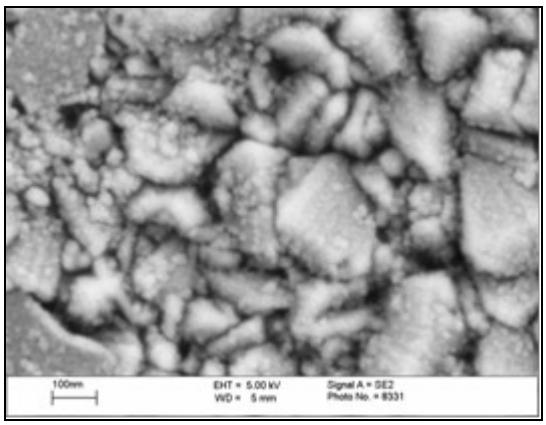

Fig.1 SEM picture of gold nano particle embedded SnO_2 film

I-V characteristic curves given in figure 2 shows the variation of photocurrent and photovoltage of the cells loading different amount of gold on the Au/SnO_2 composite film. Introduction of gold to the composite gradually increases the photocurrent and photovoltage of the cells and photovoltage and photocurrent of the cell reaches its maximum when the gold content of the Au/SnO_2 film is $1.4x10^{-3}$ % by weight. Further increment of gold in the composite film decreases the photocurrent of the cells keeping the photovoltage at the maximum voltage of 600 mV.

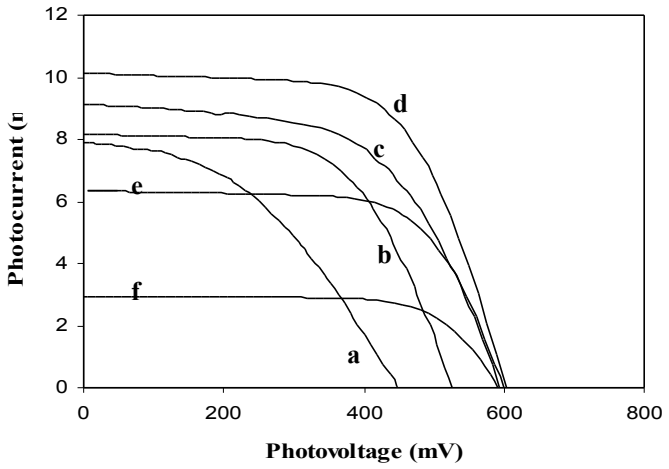

Fig. 2 I-V characteristic curves of dye-sensitized solar cells of Au/SnO_2 composite films made of (a) 0 % (b) $4.7x10^{-4}$ (c) $9.4x10^{-4}$ (d) $1.41x10^{-3}$ (e) $1.88x10^{-3}$ (f) $2.35x10^{-3}$ of gold by weight.

Study of charge transport and carrier lifetime in Au/SnO_2 and bare SnO_2 films helped to clarify the enhanced photovoltaic action in gold embedded SnO_2 films. For this purpose diffusion coefficient and lifetime of electrons in the films of SnO_2 and Au/SnO_2 of DSSC were calculated and compared. The lifetime and diffusion coefficient of electrons were measured with the intensity modulated photovoltage spectroscopy (IMVS) and intensity modulated photocurrent spectroscopy (IMPS) respectively [4-6]. Figure 3 shows the set up used to take these measurements.

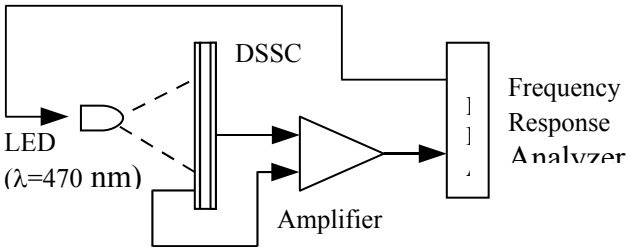

Fig 3 Schematic diagram of experimental set up for IMVS and IMPS measurements

In the IMVS measurements the solar cell is kept open circuited and the phase lag associated with the relaxation of the electrons until their recombination is observed at different intensities. Therefore the IMVS response curve is a semicircle in the lower quadrant of a complex plot with $\omega_{mim} = 1/\tau_n$ where ω_{mim} is the angular frequency at the minimum. The electron lifetimes, τ_n calculated at different intensities for those two types of the cells are given in figure 4. It is very clearly seen that for a particular intensity the lifetime is always higher in the Au/SnO_2 solar cell. This indicates that the electron recombination processes are less in Au/SnO_2 solar cell than in the bare SnO_2 solar cell.

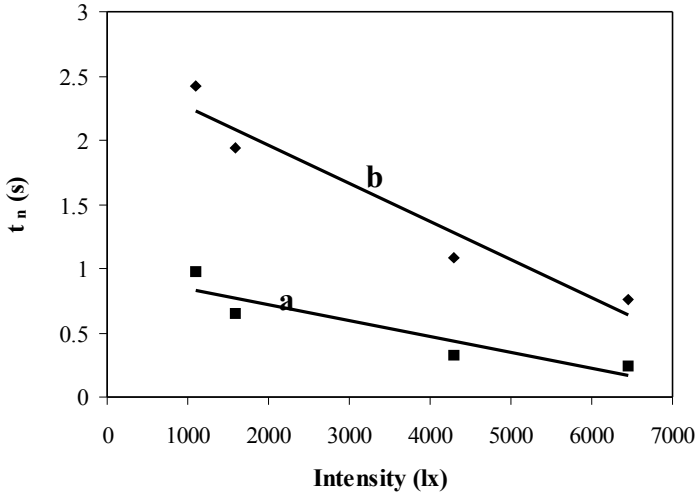

Fig. 4 Lifetime of germinated electrons in dye-sensitized solar cells of (a) SnO_2 and (b) Au/SnO_2 films at different light intensities (λ = 470 nm).

The photocurrent of the cell is also associated with a delay when the cell is short circuited when measured the intensity modulated photocurrent. The photo-generated charges take some time to diffuse to the back contact of the cell. Therefore IMPS response curve is also a semicircle in the lower quadrant of a complex plot where at the minimum of the semicircle $\omega_{mim} = 1/\tau_D$. The delay time can be estimated by the $\tau_D = d^2/4D_n$ [6]. Where d is the thickness of the film and D_n is the diffusion coefficient. An average thickness is considered here because the delay time depends on the position of the germination of the electron. Figure 5 shows the diffusion coefficient of the Au/SnO_2 and SnO_2 cell at different intensities. It is also evident from this plot that the diffusion coefficient has a higher value for the Au/SnO_2 solar cell at a particular intensity and the rate of increment of the diffusion coefficient with light intensity is rapid in the Au/SnO_2 cell.

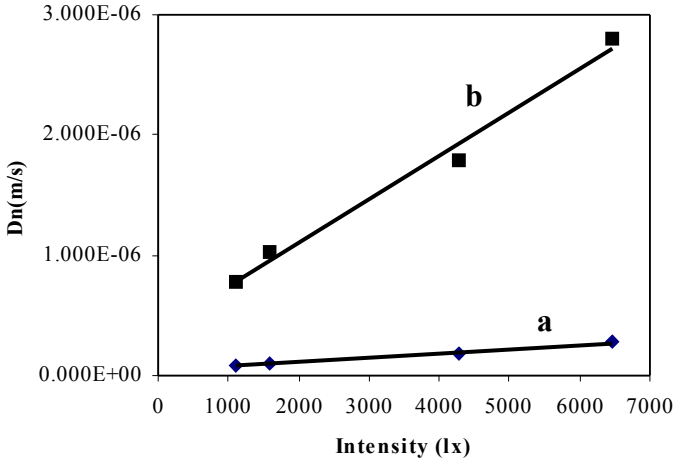

Fig. 5 Diffusion coefficient of dye-sensitized solar cells of (a) SnO_2 and (b) Au/SnO_2 films at different light intensities (λ = 470 nm)

4. DISCUSSION

It is well known that electrons transfer from the material having a higher Fermi level to the lower Fermi level matching the two Fermi levels together when a metal is in contact with a semiconductor. As a consequence, the bands of semiconductor bend at the interface forming a depletion layer, which could extend even to a maximum depth of one micrometer (figure 6b). But the situation is different at a metal semiconductor interface when the particles are

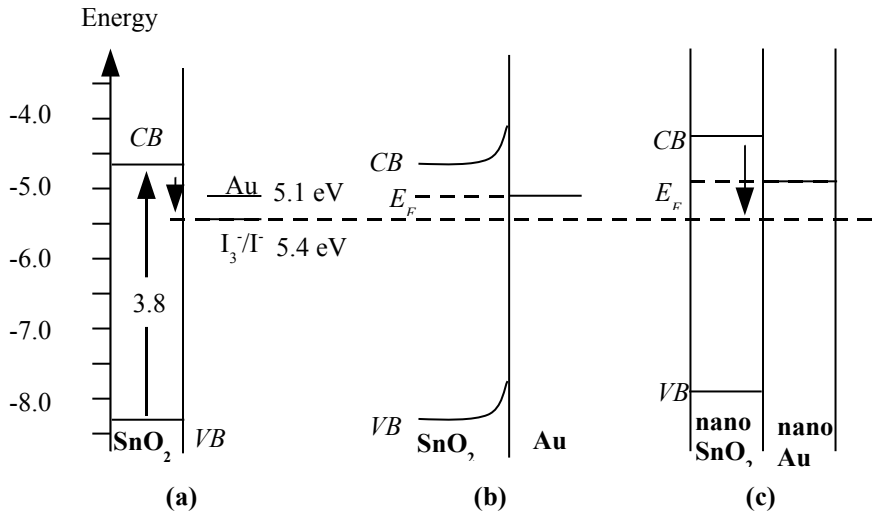

Fig. 6 Band diagram of (a) SnO_2 (b) SnO_2 and gold Schottky junction (c) SnO_2 and gold nano-particle contact.

in nano range. Build up of a depletion layer in the interface is questionable because of the small size of the semiconductor particle and the metal particle. But still their energies have to be equalized when they are in contact. Therefore electrons have to transfer from material with higher Fermi level to material with lower Fermi level even in particles of nano range. The Fermi level of SnO_2 is high compared to the work function of gold (figure 6a). Therefore electrons in conduction band of SnO_2 transfer to gold in order to gain an equilibrium energy state. Since the particles are in the nano range the potential of the conduction band edge of SnO_2 rises up in the case of SnO_2 nano particles together with the Fermi level of the Au/SnO_2 composite film (figure 6c). As a consequence the photovoltage of the cell increases because the conduction band edge of SnO_2 is now at a higher level. Shift of the conduction band edge is supposed to suppress the recombination of electrons which intern increases the lifetime of the germinated electrons in DSSC.

When electrons are injected to the Au/SnO_2 film by excitation of the dye molecules they travel across SnO_2 and Au nano-particles in the composite film. The band structure of the Au/SnO_2 film is depicted schematically in figure 7. Here electrons are supposed to transport ballistically across the gold nanoparticles in between two SnO_2 particles when the particle size of gold is comparatively small [7]. But when the gold particles graw bigger the structure become more like a multiple quantum well structure where electrons possibly fall or to trapped in the quantum wells. This is attributed to the retardation of photocurrent of the cells when the gold content in the film is increased. But this will not effect on the photovoltage so that the photovoltage of the cell remains further at the maximum value. The ballistic transport of electrons through composites increases the diffusion coefficient of electrons as well.

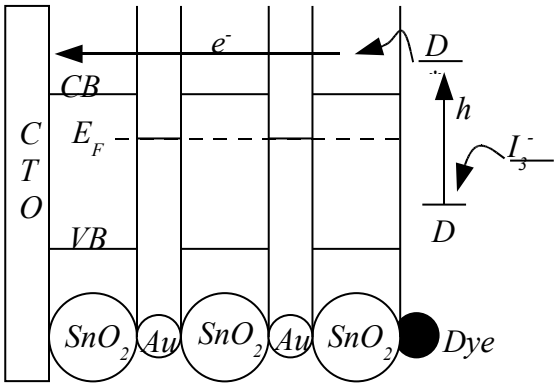

Fig.7 Schematic band diagram of Au/SnO_2 composite to illustrate electron transport through the film.

5. CONCLUSION

The present study shows that DSSC made of composite films of gold and SnO_2 of nanometer size particles enhance the charge transport and their lifetime. According to our investigation it is clearly seen that the diffusion coefficient and lifetime of electrons increases when gold nano particles are embedded in SnO_2 films of DSSC. Since it is possible to ballistically transport electrons in this structure, diffusion coefficient also increases. On the other hand the shift of the conduction band of SnO_2 when in contact with metal suppresses the recombination losses which intern increases the lifetime of electrons.

Acknowledgement: This work was financially supported by the National Science Foundation of Sri Lanka (Grant: RG/2004/P/03)

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