

PHOTOVOLTAIC PERFORMANCE OF Ag@TiO₂ CORE SHELL

Ye Hlyan Win¹, Yin Maung Maung² and Than Than Win³

Abstract

Silver particles were synthesized by using an aqueous-based reduction method. Silver thin film (core) was synthesized in form of finely silver films. The ITO coated glass was used as substrate for chemical bath deposition (CBD) at 120° C for 2 h. Shell material (TiO₂ solution) was coated onto Ag thin film by spin coating technique. The grain size of the Ag particles, Ag thin film and Ag-TiO₂ thin film were studied by scanning electron microscope (SEM). Optical properties of silver thin film were determined from transmittance spectrum with SHIMADZU UV-1800 spectrophotometer. Ag-TiO₂ thin film was prepared by spin coating method. The electrical properties were investigated by leakage current versus voltage (I–V) measurements. The reverse bias characteristics and the forward bias characteristics of the Schottky barrier of the Ag-TiO₂ thin film were also determined. Photovoltaic parameters: conversion efficiency (η_{con}) 4.83 % and fill factor (FF) 0.27 are also determined.

Introduction

The second-generation solar cell, which has been under intense development for the 90s and early 2000s, are low-cost thin-film solar cells. These cells use minimal materials and cheap manufacturing processes. [M.A.Green, et al(2010)] These thin materials are usually produced by physical or chemical deposition techniques, which can be applied to large areas and fast throughout. The term “thin film” refers more to the solar cell technologies with mass-production possibilities rather than the film thickness. The main advantage of thin-film solar cells is low cost due to low cost of processing and materials.[E.S.Aydil(2007)]

Polycrystalline and amorphous semiconductors contain intrinsic defects, which increase the density of traps and recombination centers, and reduce diffusion lengths. Therefore, an extended built-in electric field in low-doped absorber layer is used to aid carrier collection. The voltage dependent

¹ Dr, Lecturer, Department of Physics, Dagon University

² Department of Physics, University of Yangon

³ Department of Physics, Pinlong University

charge collection in the depleted absorber layer is the dominant charge collection mechanisms in thin film solar cells.[S.M.Sze(1981)]

Thin film technologies have gained much interest because of their potential for low cost, large area fabrication. However, this lack of long range atomic order also results in high defect densities, limiting the film thickness to values ~ 300-500 nm for efficient charge collection. Optical absorption in thin layers is generally weak at infrared wavelengths and therefore requires a light trapping mechanism to increase the path of light travel within the film. Therefore, there is an ongoing interest in improving cell efficiencies while maintaining the low-cost large area advantage of thin film technology. [P.Bermel, et al(2007)]

Thin film solar cells are what many have resorted in order to tackle this issue. This makes it feasible for large-scale production. The deposition techniques involved allow the making of certain novel compound semiconductors which otherwise wouldn't be possible. The deposition techniques are flexible enough for the deposition to be on substrates such as glass, flexible substrates, polymer substrates etc. Certain electrical and optical properties that would not have existed in case of a same single crystal structure deposition becomes available. A few of the very important deposition techniques for thin film includes thermal evaporation, sputtering, CBD (Chemical Bath Deposition), ALD (Atomic Layer Deposition) etc. However the major disadvantage of a thin film solar cell being the high density of defects in their lattices compared to a single crystal structure. [H.J.Moller (1993)]

Recently, core-shell nanowires have brought much attention because of the possibility to tune the properties of core nanocrystal with addition of the shell. By choosing appropriate core and shell materials, the emission wavelength can be tuned in a larger range than both of materials alone. [P.Shimpi, et al(2009)] Based on different band structure alignment at core and shell materials interface, there are three different systems, type I, type II, and type III. At Type I, band gap of shell materials is larger than that of core materials, in which electrons and holes will be confined within core materials. At type II, band gap of shell materials is smaller than that of core materials, in which electrons and holes will be partially or completely confined within shell

depending on how thick shell materials is. At type III, either the valence-band edge or the conduction band edge of the shell material is located in the band gap of the core. [P.Reiss, et al(2009)] Several different technology approaches have been used to build the solar devices, such as thin film solar cells, and dye-sensitized solar cells.

Low dimensional nanostructure have brought up much attention to fabricate photovoltaic devices. [T.J.Hsueh, et al(2007)] Using nanostructure materials can improve not only efficiency but reduce the cost and size. Among all the available nanostructure, recently, core-shell semiconductor nanowires have gained a lot of interests. Comparing to conventional solar cells, core-shell structure solar cells have several advantages. For example, for conventional solar cells, electrons and holes stay in same region after photoexcitation, so electrons and holes have larger chance to recombine again, which will decrease electronic transport efficiency.[Y.Zhang, et al(2007)]

Core-shell structure photovoltaic devices have greater carrier collection and overall efficiency because each core-shell nanostructure might have high aspect ratio which allows optimal light absorption and carrier extraction into orthogonal spatial directions.[B.M.Kayes, et al(2005)]

Experimental

Silver nanoparticles were synthesized by an aqueous-based method. Silver nitrate was taken as the metal precursor. For the synthesis of silver particles, silver nitrate (AgNO_3) and deionized water were used as metal precursors. In a synthesis, 10mmol of silver nitrate was dissolved in 10ml of deionized water. The pH of the solution was adjusted to about 9 by adding drop by drop solution of sodium hydroxide (NaOH). Ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) was also used as a stabilizing agent. Then the solution was heated with water bath at 80°C until the solution evaporated. The co-precipitated precursor required a calcination at 600°C for 1:30 h, in order to be developed into a high purity silver particles.

Core material (Ag thin film) was prepared by mixing 0.0764 g of silver nitrate (AgNO_3) and 0.1 g of (NaCl) with 50 ml of dehydrates iodine water (DIW). First solution was stirred by magnetic stirrer to dissolve completely. And then, 10 ml of Ethylene glycol (EG) and 50 ml of DIW were

added into 0.564 g of polyvinylpyrrolidone (PVP). Second solution was stirred by magnetic stirrer to dissolve completely. After they dissolved completely, first and second solutions were mixed. The ITO glass substrate was deposited in that mixture solution by chemical bath deposition(CBD) at 120 ° C for 2 h. To form the fine Ag films, Ag glass substrates were annealed at 400 ° C for 1h.

TiO₂ used as a shell material to fabricate core-shell thin film. TiO₂ sol-gel solution was formed from mixture solution of TiO₂ and methanol by stirring with magnetic stirrer for 1.5 h with 600 rpm. Finally, the Ag-TiO₂ core-shell thin film was done by coating TiO₂ sol-gel solution on Ag thin film.



(a) Silver (Ag) nano particles



(b) Ag thin film annealed at 400° C



(c) Ag-TiO₂ thin film annealed at

Figure 1: Sample preparation procedure

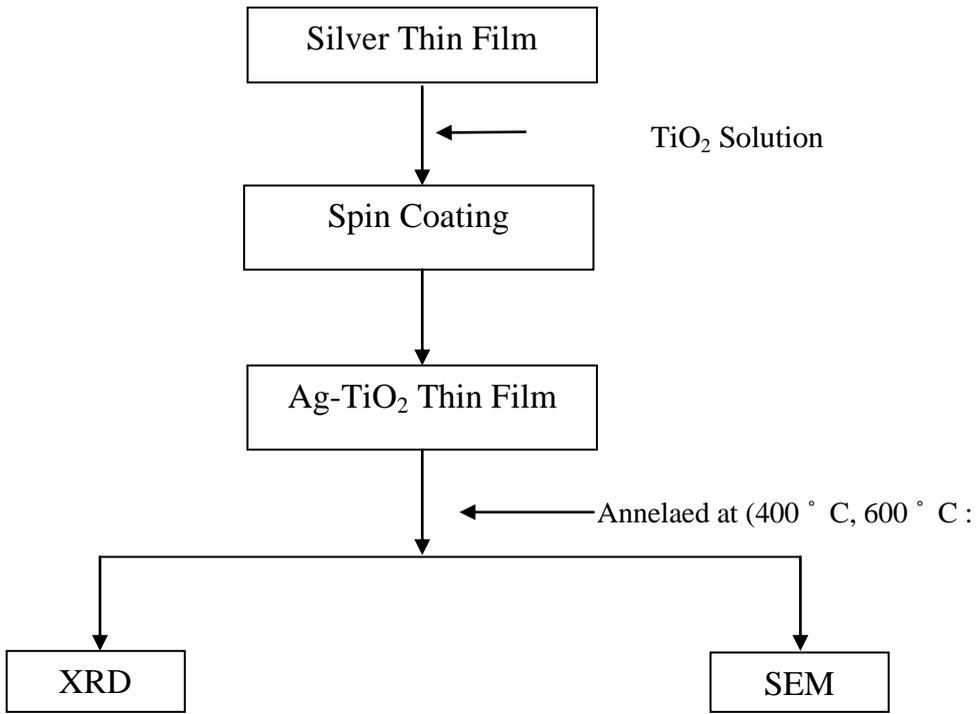


Figure 2: Block diagram for preparation of silver particles

Results and Discussion

Ag film was thus formed onto glass substrate by chemical bath deposition method. XRD analysis was undertaken to examine the crystal structure and phase formation of Ag film. According to the XRD pattern of Ag film at 400 ° C, (111) and (200) diffracted peaks represented the Ag film and some extra peaks were AgCl peaks. Thus, Ag film was formed onto glass substrate at 400 ° C.

According to the XRD pattern of Ag-TiO₂ film at 600 ° C, the intensity of TiO₂ peak (101) was increased and (004) peak was formed. It can be said that Ag-TiO₂ thin film was formed at 600 ° C. The diffraction angle (Bragg angle) (2θ) of observed and standard, lattice parameter, crystal structure of Ag-TiO₂ film at 600 ° C were shown in Table 1.

The microstructure of Ag-TiO₂ samples at the annealing temperatures of 400 ° C and 600 ° C for 1 h were examined by SEM. The recorded images of those films are shown in Fig 4. The micrograph of Ag-TiO₂ become rough after annealing 400 ° C. Fig 5 showed the microstructure of Ag-TiO₂ film at 600 ° C. The grain size of TiO₂ obtained as about Ag was 0.12 μ m. It was observed that there was grain size become smaller and crack free. Among these recorded images, the film at 600 ° C was found in the most homogeneous layer. These facts are indicated the grain size and homogeneity of the films depend on the process temperature.

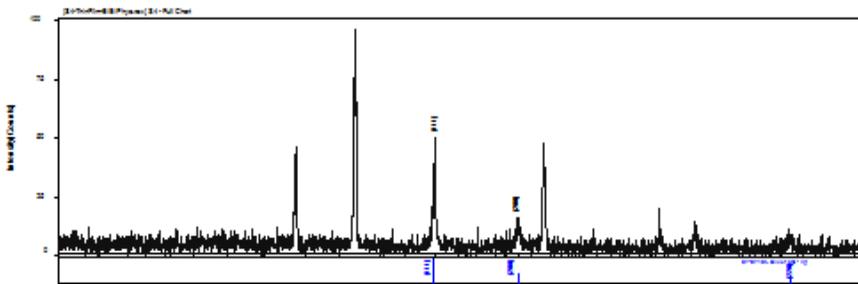


Figure 2: XRD spectrum of Ag thin film at 400 ° C

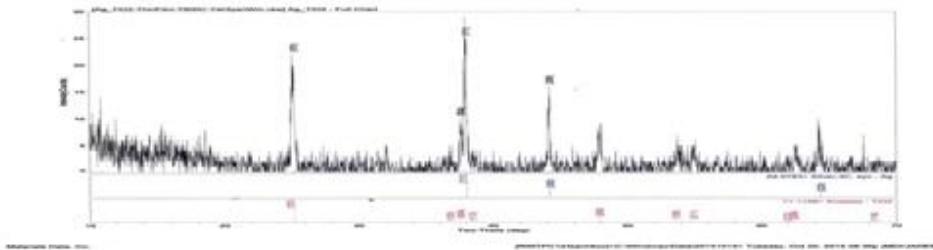


Figure 3: XRD pattern of Ag-TiO₂ thin film at 600 ° C

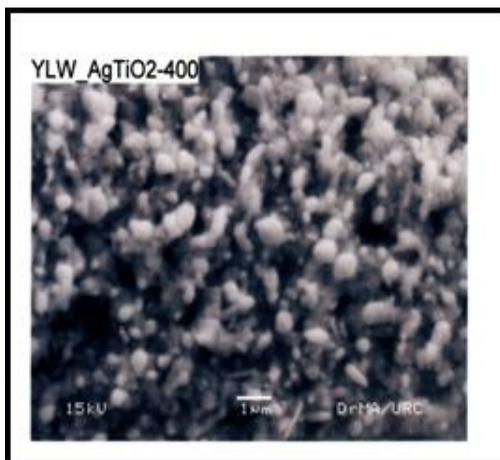


Figure 4: SEM image of Ag-TiO₂ film at 400 ° C

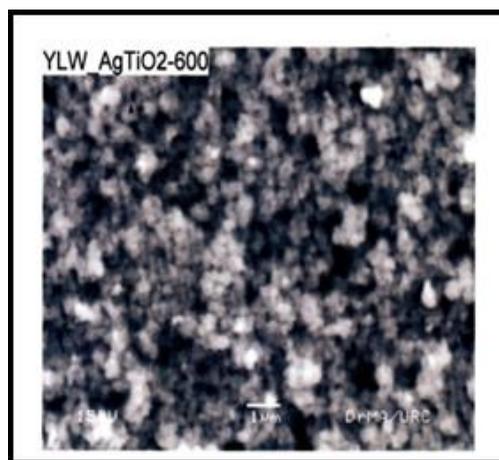


Figure 5: SEM image of Ag-TiO₂ film at 600 ° C

Table 1: Lattice parameters of Ag-TiO₂ thin films at 600 ° C

Ag	Lattice parameter (Å)	
Peaks	a	
101	4.9969	
004	4.1421	
200	4.0961	
Average lattice constant	4.3336	

TiO ₂	Lattice parameter (Å)	
Peaks	a	c
101	3.8023	9.4777
004	3.7658	9.4973
200	4.0961	9.4777
Average lattice constant	3.8844	9.4842

Table 2: Observed and standard lattice parameters of Ag-TiO₂ thin film at 600 °C

	Lattice parameter (Å)		Crystal Structure
	Standard	Observed	
Ag	4.0853	4.3336	Cubic
TiO ₂	3.74	3.8884	Tetragonal
	9.4842	9.502	

J-V Characteristics under Illumination

The performance of Ag-TiO₂ thin film defined by several parameters such as short-circuit current I_{sc} and open-circuit voltage V_{oc} obtained under illumination conditions. The output power was calculated as $P=JV$ from the J-V curves shown in Figure 8. The maximum power (P_m) of cell is then obtained. The current (I_m) and the voltage (V_m) corresponding to the maximum power point are then obtained. The photoelectrochemical parameters of Ag-TiO₂ thin film are listed in the Table 3. Fill factor (FF) under illumination condition is a measure of a diode behavior of the cell. It is obtained using a current-voltage characterization as follows

$$FF = \frac{J_m \times V_m}{V_{OC} \times J_{SC}} = \frac{P_m}{V_{OC} \times J_{SC}}$$

The efficiency η describes the overall performance of the thin film solar cell. It is defined as the ratio of P_m to the power of incident radiation (P_{in}). The maximum output power was to be found 0.103 mW/cm² for Ag-TiO₂ thin film.

The power conversion efficiency of energy to electricity conversion efficiency (η) of the cell with P_{out} electrical power under illumination condition is given by:

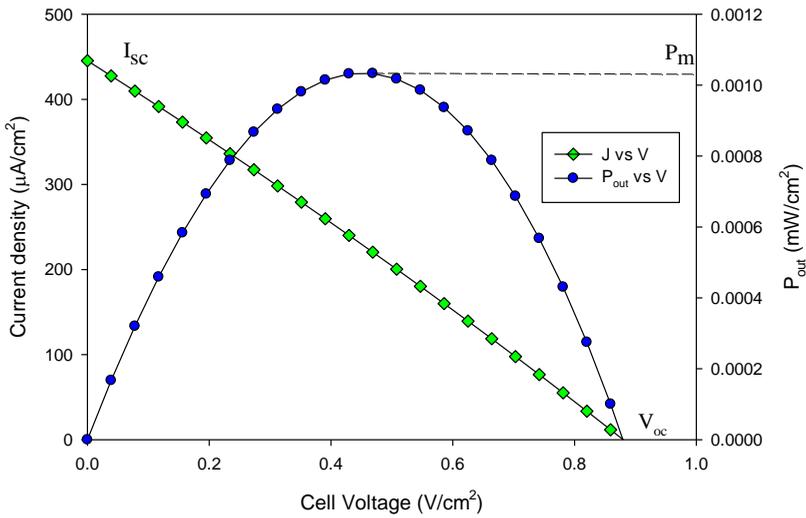


Figure 6: Current density Vs cell voltage curves for Ag-TiO₂ thin film

Table 3: Photovoltaic parameters of Ag-TiO₂ thin film

Thin film	I _m (A)	V _m (mV)	J _{sc} (µA)	V _{oc} (mV)	P _m (mW/cm ²)
Ag-TiO ₂	2.20E-04	468.8	4.45E-04	859.4	0.103

Table 4: Efficiency and fill factor of Ag-TiO₂ thin film

Thin film	η _{con} (%)	FF
Ag-TiO ₂	4.83	0.27

I-V measurement (under dark condition)

Dark current-voltage (dark I-V) measurements are commonly used to analyze the electrical characteristics of solar cells, providing an effective way to determine fundamental performance parameters without the need for a solar simulator. I-V characteristics of Ag-TiO₂ thin film are measured within the bias voltages. I-V characteristics of Ag-TiO₂ thin film is measured in the region of -5 V to +5 V by using Cu-electrode. Ln I-V characteristics obey the linear relationship and I_s was obtained by extrapolating the variation line in

which $I_s = \exp$ (intercept) relation is used. The forward applied voltage ranges, the ideality factor (η), zero bias barrier height (ϕ_{bo}) are measured by the following equations:

$$I_s = AR^*T^2 \exp\left(\frac{-q\Phi_{bo}}{kT}\right)$$

$$\frac{1}{\eta} = \left(\frac{1-\eta\Phi_{bo}}{\eta V_f}\right)$$

The zero bias barrier height and ideality factor of the Ag-TiO₂ film are listed in Table 5.

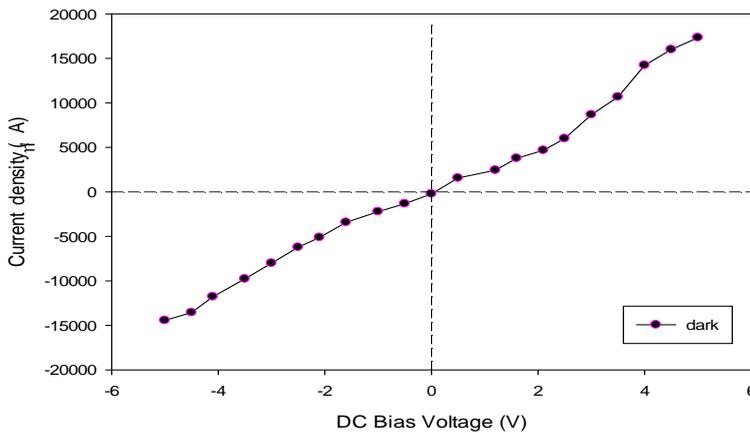


Figure7: I-V characteristics of Ag-TiO₂ thin film (under dark condition)

Table 5: Saturation current (I_s), zero bias barrier height (ϕ_{bo}) and ideality factor (η) of Ag-TiO₂ thin film

Thin film	I_s (μ A)	ϕ_{bo} (mV)	η
Ag-TiO ₂	4.26	0.2834	1.2843

Conclusion

Ultrafine silver particles in cubic form have been successfully prepared by aqueous-based reduction method. The Ag film was formed onto glass substrate at 400 ° C. It is confirmed that the temperature treated at 400° C is more suitable for silver fabrication mechanism. Growth of Ag films and their characterizations (SEM & UV-Vis) have been implemented. Moreover, it was obvious that Ag film was clearly formed onto glass substrate at temperatures 400° C. From the optical properties (UV- Vis) spectroscopic measurement, the absorption edge (major peak) position was 471 nm for Ag film at 400° C. This value was found to be within the range of acceptable value for visible light. Nevertheless, all optical band gaps in this study are ranged between the standard value of silver (1.3-2.4 eV). According to (SEM) analysis, the grain size and homogeneity of Ag-TiO₂ thin film varied with annealing temperature. Minimum grain size, homogeneous layer and uniform pores are observed at a process temperature 600° C. I-V characteristics of Ag-TiO₂ thin film are measured in the region of -5V to +5V. In the dark condition, thin film displays regular diode like characteristics with the curve passing through the origin. According to ln I-V characteristics, the measurements of saturation current, zero-bias barrier height and ideality factor are also studied. I-V curve of fabricated Ag-TiO₂ thin film are found to be p-n contact between metallic (Cu) electrode and film. Photovoltaic parameters: conversion efficiency (η_{con}) 4.83 % and fill factor (Ff) 0.27 are also determined. The growth chemistry of Ag-TiO₂ film preparation are quite acceptable for thin film fabrication manufacture although the methods employed in this work are non-expensive, non-modernized and non-complicated methods. According to experimental results, the fabricated Ag-TiO₂ (core-shell) thin film is quite suitable for photovoltaic applications.

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