Fabrication and Spectroscopic Ellipsometry Measurement of SnO_2:F Thin Film

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Abstract- Transparent and conducting oxide (TCO) glass electrode is the essential part of solar cell system. Fluorine-doped tin oxide (SnO2:F) thin film is one of the TCO layers on glass substrate. Indium-doped tin oxide (SnO2:In) (ITO) has high transparency and high electrical conductivity. But the electrical resistance of ITO increases more than three times of former value when the film temperature is 300oC or higher. So, SnO2:F (FTO) is more attractive than ITO for dye-sensitized solar cell. In this work, spray pyrolysis deposition technique was used to fabricate SnO2:F film on glass substrate. And then film thickness and refractive index of SnO2:F thin film were determined by spectroscopic ellipsometer.

Index Terms- DSSC, ellipsometer, FTO, ITO, spray pyrolysis, TCO

I. Introduction

Large amount of carbon dioxide emission by the combustion of fossil fuel leads to serious environmental problem such as the global warming. In nuclear power stations, no viable method has been found to dispose of the dangerous nuclear fuel wastes yet. So, the searching for clean and sustainable energy resources as substitute for the traditional fossil fuel and nuclear power station, has become an urgent work for human beings. Solar energy is regarded as one of the perfect clean energy resources.

Devices that will permit direct conversion of sunlight to electricity are called photovoltaic solar cells[1][3][7]. The first and second generation photovoltaic cells are mainly constructed from semiconductors. Amorphous semiconductor is one of the most promising materials for low cost energy production. But the price of solar energy from silicon technology or thin film solar cells exceeds that from the traditional fossil fuel. So, the searching for affordable solar energy technology is one of the hottest research fields all over the world. Among them, dye-sensitized solar cell (DSSC) gives the high energy conversion efficiency. Therefore, DSSC has been regarded as the most prospective clean energy source.

Dye-sensitized solar cell (DSSC), invented in 1991 by Prof. Michael Graetzel in Switzerland, is a real revolution in solar energy after the invention of silicon solar cell. Anatase TiO_2, wide band gap metal oxide semiconductor, on transparent conducting oxide (TCO) layer acts as electron acceptor, iodine electrolyte as electron donor or source for electron replacement and photochemical pumping device is dye sensitizer and carbon layer serves as a catalyst, shown Fig 1.1[4][5].

Film thickness and refractive index of TCO layer are very important factors on solar cell efficiency. Film thickness depends on the deposition time and the distance between spray gun nozzle and the glass substrate. The velocity and the feed-rate of the solution should be carefully controlled by the control button of the spray gun. In this work, spray pyrolysis technique is the simplest method for the deposition of SnO_2:F thin film. Film thickness and refractive index of the film were analyzed by Ellipsometer and those of TCO layer for TiO_2 based DSSC were studied to improve the performance of dye-sensitized solar cell. DSSC with cost-effective SnO_2:F layer can yield satisfactory efficiencies.

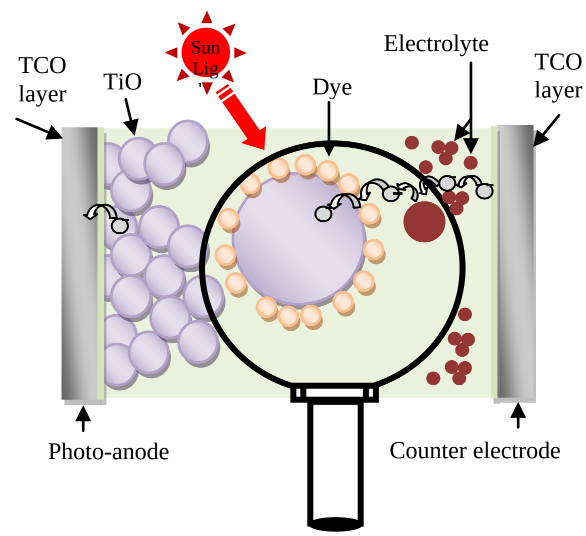

Fig 1.1 Structure of TiO_2 based dye-sensitized solar cell

II. BACKGROUND THEORY

2.1. Spray Pyrolysis Technique

Film coating on a glass substrate by spray pyrolysis technique and photograph of the spray pyrolysis apparatus[6] are shown in Fig 2.1 and Fig 2.2 respectively. It contains air compressor, spray gun, heater and digital temperature controller with temperature sensor. Glass cleaning is essential for the nucleation centre of growth, good adhesion and uniform deposition of the film. After that, the glass substrate is put on the

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heater at 600°C for FTO. The distance between the spray gun nozzle and the glass substrate can be adjusted.

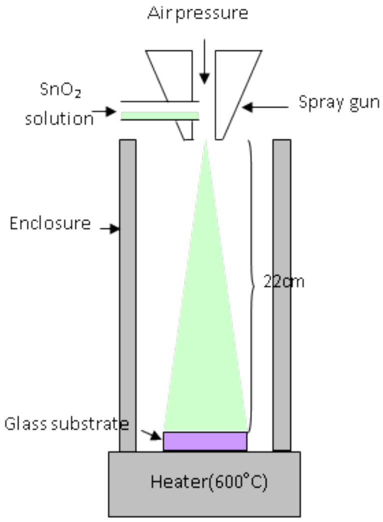

Fig 2.1 Spray pyrolysis technique

Fig 2.2 Photograph of pray pyrolysis apparatus

2.2. Spectroscopic Ellipsometry (SE) Measurement

Spectroscopic Ellipsometry (SE) is the sensitive optical technique for measuring the thickness and the optical properties of the films such as the refractive index and the absorption coefficient and so on. The thickness of the film can be determined by measuring the difference between two reflections. The change in polarization of the reflected lights is used to calculate the refractive index and the absorption coefficient.

As shown in Fig 2.3, p-polarized axis is parallel to the plane of incidence and s-polarized axis is perpendicular to it. After the reflection through thin film, the reflected lights, travelling in the same direction, combine into a wave which becomes elliptical polarized ***E*** field vector. The shape of the electric field is the polarization of reflected light and the size of the electric field means the intensity of reflected light. If the refractive index of the film and that of the substrate are known, it is possible to calculate the thickness *d* of the film by ellipsometry[2][8].

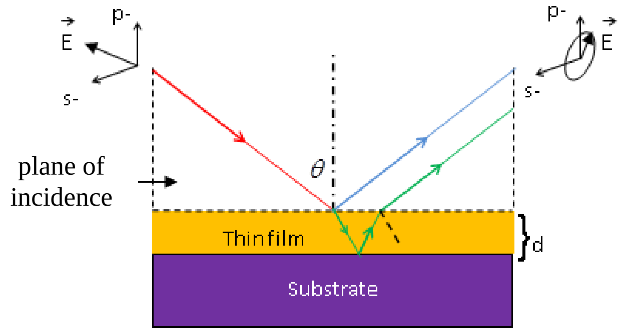

Fig 2.3 Ellipsometry experiment

Fig 2.4 shows photograph of spectroscopic ellipsometer. At first an optical model that describes the sample structure was built and the theoretical data from the optical model that corresponds to the experimental data were generated. And then the generated data were compared with the experimental data. Mean Squared Error (MSE) or Regression Analysis was used to vary unknown parameters and minimized the difference between the generated and experimental data. Ellipsometry is an indirect method for the calculation of the thickness and the refractive index of the film. In this work, the film thickness and refractive index of FTO were analyzed.

Fig 2.4 Photograph of spectroscopic ellipsometer

III. EXPERIMENTAL DETAILS

3.1 Fabrication of Fluorine-doped Tin Oxide (FTO) Glass Substrate

10 g of tin chloride pentahydrate ($SnCl_4.5H_2O$) was dissolved in 100 ml of ethanol in a sealed container[9]. The solution (A) was stirred continuously with magnetic stirrer for at least 5 h until all $SnCl_4.5H_2O$ completely dissolved as shown in Fig 3.1. In Fig 3.2, the solution (B) was prepared by dissolving 2.0 g of ammonium fluoride (NH_4F) in 4 ml of deionized water in a sealed container and stirred for 30 min. After that, the solution (A) was placed in a water bath and heated at 40°C and stirred for 1 h as shown in Fig 3.3. And then the solution (B) was added to the solution (A) in water bath, and then stirred the mixed solution at 60°C for 9 h, shown in Fig 3.4. When it

became homogeneous, it was filtered using paper filter and was to be used for SnO_2 film fabrication.

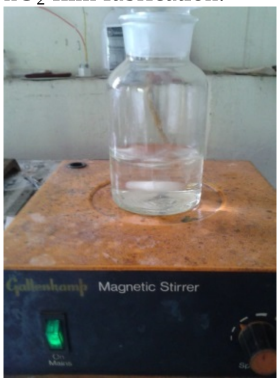

Fig 3.1 $SnCl_4.5H_2O$ solution

Fig 3.2 NH_4F solution

Fig 3.3 $SnCl_4.5H_2O$ solution in water bath at 40^oC

Fig 3.4 Mixed solution $SnCl_4.5H_2O$ and NH_4F in water bath at 60^oC

The glass slides have to be cleaned by degreasing them in acetic acid and washed with distilled water, and then cleaned with acetone and dried in air. As shown in Fig 3.5, the glass substrate was put on the heater at 600^oC. The distance between the spray gun nozzle and the glass substrate was about 22 cm and the solution feed-rate was 5 ml min^{-1}. The deposition time of each substrate took about 10 minutes. The feed-rate of the solution should be carefully controlled by the control button of the spray gun, and the direction of the solution was needed to reach the target glass. After the deposition, the glass with $F:SnO_2$ thin film should be checked by using the digital multi-meter whether conductive layer or not. The film resistance is 22.9 Ω/cm, shown in Fig 3.6.

NH_4F solution

Fig 3.5 SnO_2:F coating by spray pyrolysis

Fig 3.6 Conductive layer of FTO

3.2 Spectroscopic Ellipsometry Analysis

Film thickness and refractive index of FTO were analyzed by spectroscopic ellipsometer. At first, the optical model that describes the sample structure was built and the theoretical data from the optical model that corresponds to the experimental data were generated. And then the generated data were compared with the experimental data. Unknown parameters in optical model were varied to try and produce a "best fit" to the experimental data. Mean Squared Error (MSE) or Regression Analysis was used to vary unknown parameters and minimized the difference between the generated and experimental data. Fig 3.7 shows the regression analysis of spectroscopic ellipsometry for FTO. Table (3.1) is the refractive index with various wavelengths. In this work, the film thickness of FTO is 848.11 nm. And the refractive index of FTO is about 1.99 as shown in Fig 3.8.

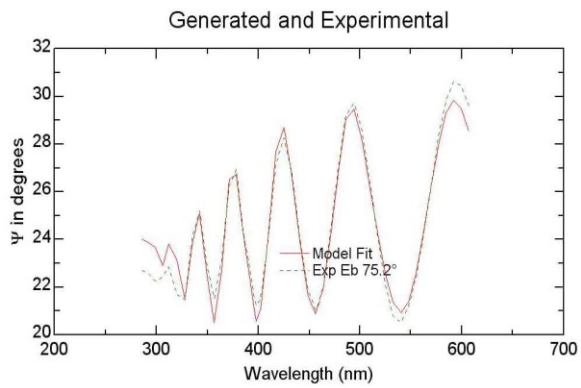

Fig 3.7 Ellipsometry measurement of FTO

Table (3.1) Refractive index of FTO with various wavelengths

λ (nm)	n	λ (nm)	n
286.0	2.0233	448.8	1.9715
291.5	2.0569	456.1	1.9702
299.0	2.0797	464.2	1.9677
306.0	2.0821	471.5	1.9662
312.0	2.0740	479.2	1.9655
320.8	2.0539	486.4	1.9654
327.8	2.0378	494.4	1.9659
335.1	2.0258	502.4	1.9675
342.4	2.0181	510.0	1.9687
349.5	2.0135	517.6	1.9695
356.8	2.0083	525.0	1.9698
364.0	2.0022	532.5	1.9709
371.3	1.9947	540.4	1.9721
378.4	1.9878	547.9	1.9726
384.5	1.9827	555.5	1.9725
397.5	1.9726	563.2	1.9717
402.1	1.9705	570.7	1.9708
409.7	1.9687	577.9	1.9703
417.2	1.9686	585.0	1.9711
424.9	1.9687	592.3	1.9746
432.8	1.9702	599.7	1.9819
440.7	1.9715	607.0	1.9939

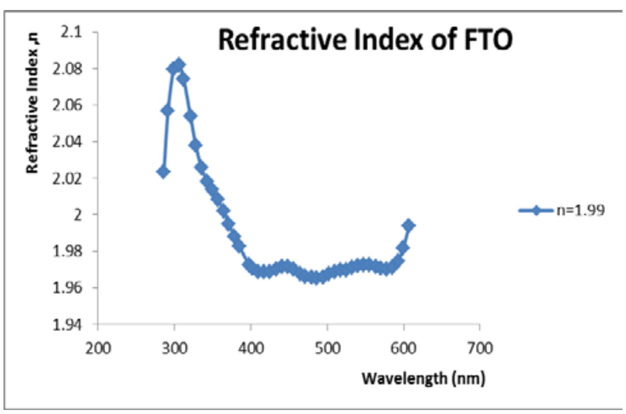

Fig 3.8 Refractive index of FTO

IV. RESULTS AND DISCUSSION

4.1 Spectroscopic Ellipsometry Study

Ellipsometry is the indirect method for the calculation of thickness and refractive index of thin film. The parameters Psi(Ψ) and Delta(∇) have to be analyzed and fitted to determine the thickness and the refractive index of the film. In this process, the optical model with generated data has to be built first to compare with the experimental data. And then the difference between generated data and experimental data must be minimized by using regression analysis. FTO thickness 848.11 nm is larger than the optimum value. This is because that the deposition time should be less than 10 minutes and the feed-rate of the solution should be also reduced by using the control button of the spray gun. FTO refractive index, about 1.99 means that the solution needs to be more homogeneous. But the high refractive index is needed for the use of more refraction, but low value for the less refraction. After that the film resistance 23 Ω/cm can be practically used in DSSC. The film resistance, depends on the materials used in deposition, needs to reduce as much as possible to increase the efficiency of DSSC. In this work, the optimum deposition temperature of FTO is 600°C. For TiO_2 based DSSC, TiO_2 glass electrode will be deposited on FTO glass substrate at 450°C. So, FTO deposition temperature must be greater than TiO_2 layer deposition temperature.

V. CONCLUSION

TCO glass electrode is the essential part of DSSC. Low electrical resistivity and high visible transmittance are the key elements for TCO layer. The film thickness and the refractive index of FTO have been studied by SE measurement. The film thickness depends upon the deposition time and the feed-rate of solution. According to SE data, the refractive index is 1.99 and the film thickness is 848.11 nm. To get the optimum film thickness, the solution feed rate and the deposition time should be reduced.

TiO_2 coated photo-anode on FTO layer has to be prepared for TiO_2 based DSSC. In this work, FTO deposition temperature is about 600°C. So, FTO deposition should be put emphasis on the film deposition temperature and the film thickness. And then glass cleaning with acetone and methanol, is an essential process to get good adhesion and uniform deposition for FTO film. More homogeneous SnO_2:F solution should be provided to get uniform thin film. So, the stirring time of the solution and the solution preparation temperature should be adjusted to get homogeneous film[7].

To improve the performance of DSSC, the conductive layer resistance of FTO, about 22.9 Ω should be reduced to a smaller one.

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