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Reflectance enhancement by multi-layered TiO_2/SiO_2 coating on stainless steel substrate for dye-sensitized solar cells

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$[TiO_2|SiO_2]$ multi-layer for the DSSC was fabricated to improve the light re-adsorption of the dye by the enhancement with the light reflectivity from the surface of stainless steel substrate. TiO_2 (H) and SiO_2 (L) thin films were deposited on the stainless steel substrate by RF magnetron sputtering at a high substrate temperature of 600 °C and multi-layer structure of $[air|(HL)^4|304SS]$ was fabricated. In order to estimate high reflection coating and the experimental results in advance, the simulation program, the Essential Macleod Program was adopted. SiO_2 thin film showed the low refractive index of 1.6259 and TiO_2 thin film showed high refractive index of 2.4722 at a wavelength of 633 nm measured by ellisometry measurement. The spectral reflectance of stainless steel increased up to around 75% by multi layer optical coating at a wavelength range of 400 - 550 nm.

Key words: Reflectance, Coating, EMP, RF sputtering.

Introduction

Thin film optics, which is based on light interference phenomenon [1], is extensively employed as anti-reflection [2], high reflection [3] and bandpass filter [4] in the development of optical, electronic and solar industries. Among them, the high reflection coating significantly enhances the reflectivity of the surface in the certain wavelength range. The coating can be designed as a long or short-pass filter or a mirror with a specific reflectivity [2, 4]. In this view, the reflectance on the metal substrate could be enhanced by depositing dielectric multi layers which have high and low refractive indexes with managing the thickness and the number of layers.

The stainless steel is generally used as a substrate and reflector in the flexible dye-sensitized solar cell (DSSC). However, it shows low spectral reflectance of around 50 - 60% in the visible wavelength range. It is assumed that the efficiency of the flexible DSSC will be improved with the increase with the light reflectivity on the reflector since re-absorbed amount of light reflected from reflector is enlarged. It is feasible to enhance the surface reflectivity of stainless steel efficiently with high reflection coating in the flexible DSSC because the light is mainly absorbed by the dye at the wavelength range of 400 - 550 nm according to the incident photon-current conversion efficiency (IPCE) [5].

So far, a number of experimental researches have been successfully conducted in the area of the structural and optical properties of the flexible DSSC [6-8], However, not many works have been undertaken to estimate in terms of the enhancement with the light reflectance on the reflector [9, 10].

This work aims to understand and evaluate the phenomenon of high reflection coating on the stainless steel and to investigate a possible application for DSSC. In order to estimate and compare with the experimental results, the simulation program, the Essential Macleod Program, was adopted. For this purpose, $[TiO_2|SiO_2]^S$ multi-layer for high reflection coating was deposited on the stainless steel substrate at a high substrate temperature of 600 °C by RF magnetron sputtering method based on the simulation results.

Experimental

Simulation

One of the optical programs named Essential Macleod Program (EMP) was adopted to simulate the optical characteristics such as transmittance, reflectance and colors in advance through the variety of thickness, structure and materials in the multi layer thin films.

The EMP was processed through the following steps; first, construction parameters such as refractive index and extinction coefficient of TiO_2 and SiO_2, which were calculated by ellipsometry measurement, were input in the program. Second, $[Air|(TiO_2|SiO_2)^S|304SS]$ multi-layers were designed and simulated with various parameters such as wavelength ranges (380 - 780 nm), thickness (20 - 200 nm) and layers of structure (S = 1 - 10). Finally, analysis on the parameter effect was performed with system modification for optical properties whether it is appropriated for the optimum simulation.

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Films preparation

The cut stainless steel sheets (304SS, 10×10× 0.3 mm^3) were ultrasonically cleaned with acetone, absolute ethyl alcohol and de-ionized water for 30 minutes. Using 2 inch TiO_2 (99.99%) and SiO_2 (99.99%) ceramic target as the sputtering source, TiO_2 and SiO_2 thin films were deposited on the 304SS in order of precedence under the following parameters: 50 sccm in Ar flow rate and 5 sccm in O_2 flow rate, 13 mTorr in working pressure, 150 Watt in RF sputtering power for TiO_2 and SiO_2 target at 600 °C substrate temperature. The thicknesses of TiO_2 and SiO_2 layers were controlled by increase in the sputtering time at constant optimized conditions.

Characterizations

The monolayer thickness was measured using a surface profiler meter (α-step, TENCOR P-2). The crystal structure was determined by X-ray diffractometer (D8 Discover with GADDS, Bruker AXS). Field emission scanning electron microscope (LEO-1530, Carl Zeiss) was used for micro-structural examination and thicknesses. The refractive index n and the extinction coefficient *k* were evaluated by ellipsometry measurement using ellipsometer (Elli-SE) in the visible range from 350 to 750 nm with a step width of 5 nm. The spectral reflectance of multi layer thin film was estimated using a spectrophotometer (CM-3600d, MINOLTA) with a light source of D65.

Results and discussion

Fig. 1 showed XRD patterns of TiO_2 thin films and SiO_2 thin films fabricated at different substrate temperatures. Fig. 1(a) represented the tendency of the crystallinity in TiO_2 thin films with an increase of substrate temperatures from 200 °C to 600 °C, respectively. TiO_2 thin film deposited at 200 °C observed as an amorphous state due to low substrate temperature during RF sputtering process. In the substrate temperature above 300 °C, TiO_2 thin films observed exhibited TiO_2 rutile crystalline phase. And peak intensity increased with (110) preferred orientation at 2θ = 32.196 ° with an increase of substrate temperatures from 300 °C to 600 °C and the strongest rutile peak was appeared on the substrate temperature of 600 °C Fig. 1(b) showed XRD patterns of SiO_2 thin film deposited on the substrate temperature of 600 °C SiO_2 thin film showed the amorphous phase with an increase of substrate temperatures from 200 °C to 600 °C.

The cross sectional SEM images of monolayer TiO_2 and SiO_2 thin films fabricated at a substrate temperature of 600 °C presented in Fig. 2. It could be confirmed that thicknesses of TiO_2 and SiO_2 thin film were 113.4 nm and 118 nm, respectively.

To extract an accurate analysis from the EMP simulation, the refractive index and the extinction coefficient are necessary. Fig. 3 showed the refractive index *n* and extinction coefficient *k* of crystalline TiO_2

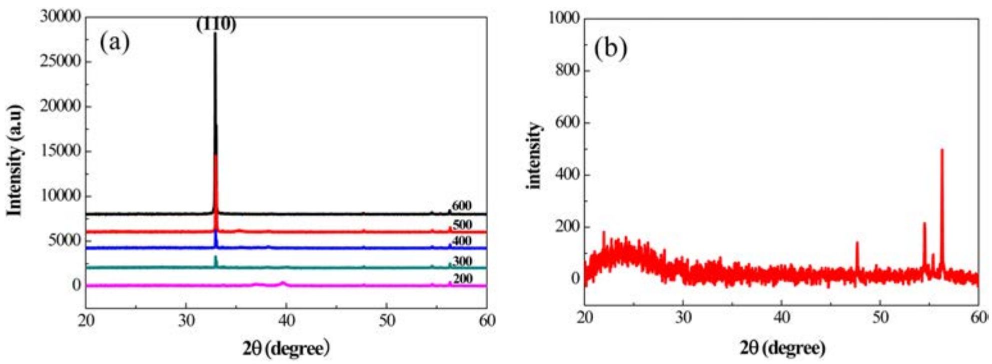

Fig. 1. XRD patterns as a function of substrate temperature; (a) TiO_2 thin film and (b) SiO_2 thin film.

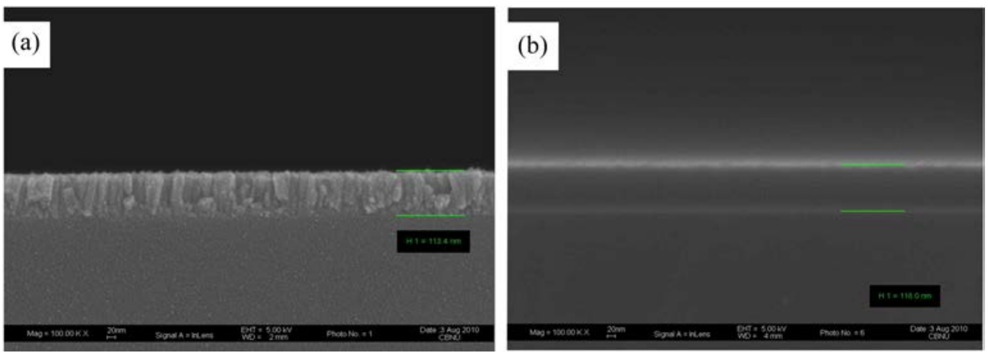

Fig. 2. Cross sectional SEM images of (a) TiO_2 thin film and (b) SiO_2 thin film.

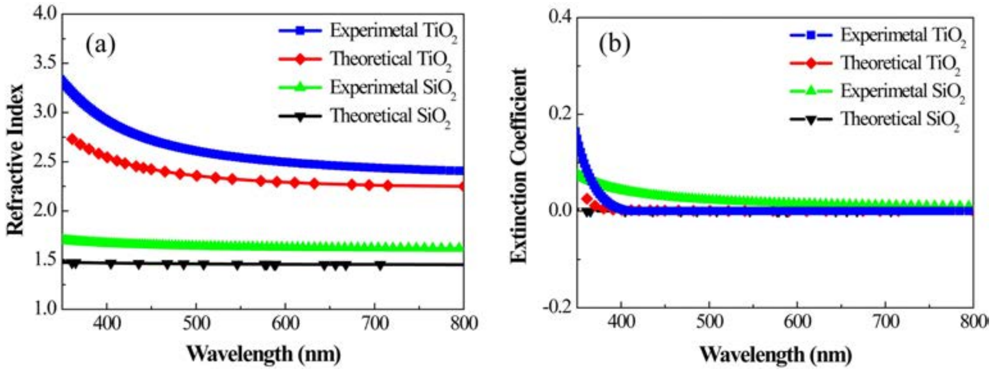

Fig. 3. (a) The refractive index n and (b) extinction coefficient k with TiO_2 and SiO_2 thin film in the visible range using ellipsometry measurement.

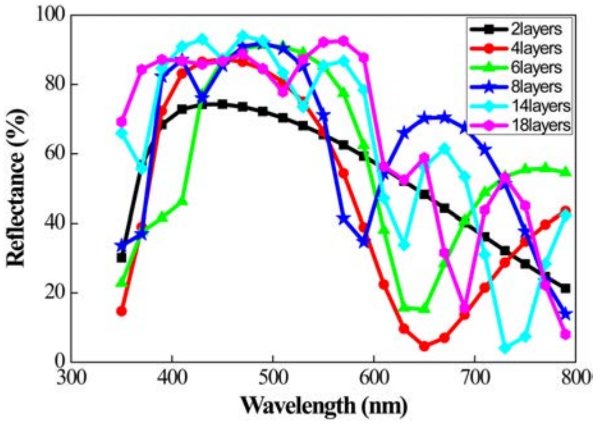

Fig. 4. Comparison of simulated spectral reflectance with different S values for [air|(HL)^S|304SS] multi-layer thin films; S = 1, 2, 3, 4, 7 and 9.

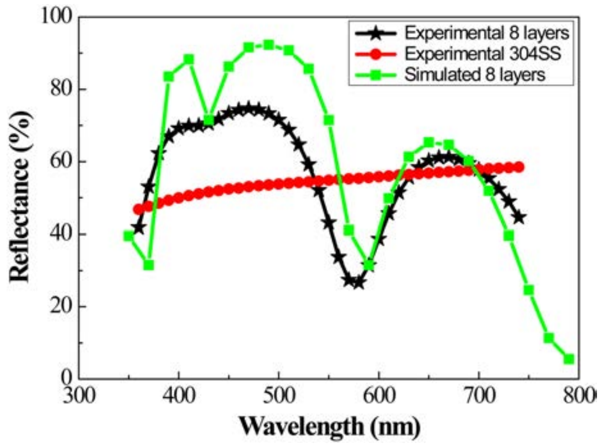

Fig. 5. Comparison of spectral reflectance with simulated and experimental multi layer thin films.

and amorphous SiO_2 thin films as a function of the wavelength in the visible range from 350 to 800 nm, which were obtained by the ellipsometry measurement. The measured values of TiO_2 thin film were $n = 2.4722$ and $k = 0$, which were slightly different from the theoretical values of $n = 2.2789$ and $k = 0.0002$ [11] at a wavelength of 633 nm. For this reason, it is considered that the refractive index of TiO_2 thin film was physically increased. The measured value of SiO_2 thin film were $n = 1.6259$, which were slightly increased about 0.1689 comparing with the theoretical value of $n = 1.4570$ [11] at a wavelength of 633 nm. This is possibly associated with the fact that during deposition, O_2 flow rate was relatively lower than Ar flow rate so that O_2 partial pressure in thin films was reduced [12, 13].

Optical constants of SiO_2 and TiO_2 thin film, designated as the low refractive index (L) and the high refractive index (H), were input in the Essential Macleod Program and then [air|(HL)^4|304SS] multi layer were simulated. Fig. 4 demonstrated the simulation results by managing the thicknesses and the number of layer (S) with the selective high reflectance coating, respectively.

From the simulation, [air|(HL)^2|304SS] 4-layer which indicates S = 2 showed around 80% spectral reflectance in the wavelength range of 410 - 510 nm and had the maximum peak of 87% at a wavelength of 450 nm. Also [air|(HL)^4|304SS] 8-layer which indicates S = 4 showed around 85% spectral reflectance in the wavelength range of 400 - 520 nm and had the maximum peak of 90% at a wavelength of 480 nm. In our experiment, [air|(HL)^4|304SS] was selected because it is well matched with the IPCE results that the light is mainly absorbed by the dye in the wavelength range of 400 - 550 nm and satisfied with simulation based on the optimized design.

[air|(HL)^5|304SS] and [air|(HL)^6|304SS] multi-layers showed less than 80% spectral reflectance in the wavelength range of 400 - 520 nm. Also, simulated [air|(LHL)|304SS], [air|(LH)^{S}L|304SS] and [air|(HLH)|304SS] multi-layers showed similar or lower spectral reflectance of 50 - 60% in the visible wavelength range so that they were not carried out in the experiment. Multi-layers deposited more than S = 7 indicated the lower reproducibility and reliability in experimental results.

Fig. 5 represented the spectral reflectance of experimental [air|(HL)^4|304SS] multi-layer, which is based on the simulation result, fabricated by RF magnetron sputtering. [air|(HL)^4|304SS] multi-layer demonstrated

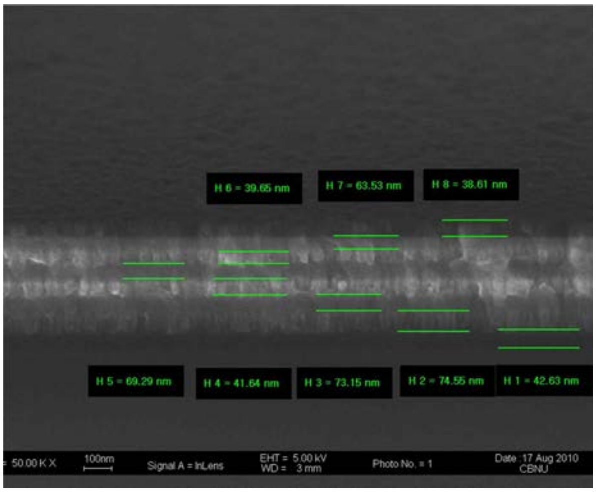

Fig. 6. Cross sectional SEM images of [air|(HL)^4|substrate] multi-layer thin film.

the spectral reflectance increased around 20% more than the bare stainless steel substrate in the wavelength range of 380 - 500 nm. Also, [air|(HL)^4|304SS] multi-layer indicated the maximum peak of 75% at a wavelength of 470 nm showed approximately 22% higher than the bare stainless steel substrate which showed 55% spectral reflectance.

Even though the curve patterns between simulated and experimental spectral reflectance were well matched, maximum and minimum peaks were indicated some of the discrepancies in the wavelength range of 380 - 580 nm. One of the reasons for this is considered as the difference in the optical constants of simulated and experimental substrate. 304SS was deposited by RF Magnetron Sputtering with bulk target and its optical constants were measured by the ellipsometry measurement and input in the simulation program. Because of this, the optical constants of 304SS between thin film and bulk could be different and attributed to the discrepancies [14]. In addition, the reflectance peaks might be deduced by the inter-diffusion in the multi-layer. The level of inter-diffusion could be increased by the deposition process at high temperature more than room temperature. Furthermore, a long-term deposition process at high temperature could slightly give variety to the deposition condition and affect the thickness of each layer, respectively.

Fig. 6 described cross sectional SEM images of experimental [air|(HL)^4|304SS] multi-layer thin film (× 50,000). Each layer indicated the distinct boundary and deposited on the surface uniformly. Table 1 showed the experimental thickness of [air|(HL)^4|304SS] multi-layer thin film and simulated value. As seen in Table 1, the experimental thickness of each layer was slightly different from simulated one so that the spectral reflectance was deemed to indicate some of the discrepancies.

Conclusions

TiO_2 and SiO_2 thin films were deposited on the stainless steel substrate by RF magnetron sputtering at a high substrate temperature of 600 °C and SiO_2(L) thin film showed the low refractive index of 1.6259 and TiO_2(H) thin film showed high refractive index of 2.4722 at a wavelength of 633 nm.

Simulated [air|(HL)^4|304SS] 8-layer which indicates S = 4 showed around 85% spectral reflectance in the wavelength range of 400 - 520 nm and exhibit the maximum peak of 90% at a wavelength of 480 nm and then [air|(HL)^4|304SS] multi-layer was fabricated based on the simulation results. Experimental [air|(HL)^4|304SS] multi-layer demonstrated the spectral reflectance increased around 20% more than the bare stainless steel substrate in the wavelength range of 380 - 500 nm. Also, experimental [air|(HL)^4|304SS] multi-layer indicated the maximum peak of 75% at a wavelength of 470 nm, indicating approximately 22% higher than the bare stainless steel substrate which showed 55% spectral reflectance.

The present study showed that optical simulations provide numerous important implications on the performance for the experimental optical characteristics of [air|(HL)^4|304SS] multi-layer at a high substrate temperature of 600 °C It can be concluded that the experimental optical properties of multi-layer were extracted the required information from the simulation results in advance and [air|(HL)^4|304SS] multi-layer could be performed as a reflector in the flexible DSSC. Also it is feasible to enhance the surface reflectivity of stainless steel efficiently by high reflection coating with [TiO_2|SiO_2]^S multi-layer in the flexible DSSC because the light is mainly absorbed by the dye at the wavelength range of 400 - 550 nm.

Acknowledgement

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Table 1. Comparison with simulated and experimental thickness of [air|(HL)^4|substrate] multi-layer.

	304SS	SiO_2 (nm)	TiO_2 (nm)	SiO_2 (nm)	TiO_2 (nm)	SiO_2 (nm)	TiO_2 (nm)	SiO_2 (nm)	TiO_2 (nm)	Air
Simulation		43	75	73	40	70	39	64	39	
Experiment		47.42	75.62	70.68	45.52	65.13	42.51	58.12	40.58	

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