Low Temperature Preparation of Nano-porous TiO_2 Layers for Plastic Dye Sensitized Solar Cells

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(Received August 11, 2003; CL-030744)

Short circuit currents for dye sensitized solar cells increased from 3.50 to 7.38 mA/cm^2 after TiO_2 layers were exposed to low-accelerating electron beam showers at room temperature. EB curing of TiO_2 layers was successfully conducted without substrate deterioration.

Dye sensitized solar cells (DSSC) have been paid great attentions for the next generation of solar cells. The photoenergy conversion efficiencies reached 10%, which is catching up that for amorphous silicon solar cells.[1] Another interest on DSSCs is the fabrication of plastic type DSSCs. The use of plastic substrates makes it possible to fabricate light weight, thin, and low cost DSSCs. Normally, temperatures more than 450 °C are required to cause necking of TiO_2 particles and to remove polymers containing in the TiO_2 pastes. Plastic substrates such as poly(ethylenetelephthalate) (PET) can not withstand the heat more than 150 °C. Therefore, low temperature heat treatment is required to fabricate necked TiO_2 particles. It has been reported that energy conversion efficiencies for DSSCs baked at lower temperatures were not as good as those baked at higher temperatures.[2–5] These results implied that energies other than heat are necessary to increase the energy conversion efficiencies. Minoura and his co-workers treated TiO_2 layers on substrates with steam in an autoclave at 100 °C and obtained a crack-free porous thick TiO_2 films.[6] They have reported 6.23% efficiency at 100-mW/cm^2 light intensity. Miyasaka and his co-workers have reported electrophoretically deposited TiO_2 layers. After TiO_2 films were post-heated at 80 °C under titanium alkoxide vapor, they have reported 4.1% energy conversion efficiency under 100-mW/cm^2 light intensity.[7] They also reported the effect of microwave irradiation at room temperature. Lindstrom and his co-workers have reported the method to form mechanically stable, electrically conducting, porous nanostructured films by compressing TiO_2 layers at around 100 °C. They reported 5.2% at 0.1 sun light intensity.[8–10]

We now propose another method to prepare TiO_2 layers at low temperatures. We employed low accelerating electron beam (EB) shower exposures. Substrates are exposed to EB showers like UV light. Conventionally employed EB shower exposure had to accelarete electrons with high voltages more than 100 kV because of pushing out electrons from windows in EB tubes. Electrons accelerated with high voltages easily pass through substrates and penetration depth of electrons was large. This damages whole plastic substrates when only surface of the substrate was aimed to modify with EB shower irradiations. Recently, thin window material for EB tubes (3-micron thick silicon film) was found. This allowed transmission of electron beams accelerated by a low voltage (25–60 kV) into atmosphere or reduced-pressure environment.[11,12] For example, by use of the EB showers with low acceleration voltages, only surfaces on the polymer films (1–2 micron) are modified. Application of this new technique was limited to polymer surface modification or curing.[13,14] Our idea is as follows; by controlling the acceleration voltage of the electrons, penetration depth of electrons is adjusted to the thickness of TiO_2 layers or TiO_2 layers + transparent conductive layers. Therefore, electron beam showers do not attack the substrates under the TiO_2 layers. From the TiO_2 density and the thickness, the acceralation voltage was set at 50 kV. As far as I know, this process has not been applied to make the necking among TiO_2 nano particles.

cis-Di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (N3) was purchased from Solaronix SA. Fluorine-doped SnO_2-layered glass plates (30 Ω/square) (SnO_2/F) were obtained from Nippon Sheet Glass Co. Ltd. TiO_2 pastes were prepared by grinding the mixture of P25, water and ethyl alcohol (0.8:1.0:1.5). Any nonvolatile material was not added. The TiO_2 paste was coated on SnO_2/F layered glass plates by using a metal mask (t: 30 μm) and was left at room temperature for 30 min. TiO_2 layers with 10 μm thickness were obtained. These substrates were exposed to electron beam showers. Single tube module chamber equipped with a miniature electron tube (Min-EB UEB-09: USHIO INC) and multitube module with 19 EB tubes (Miniature Electron Tube Min-EB UEB-04: USHIO INC.) equipped with nineteen miniature electron tubes (Min-EB UEB-04: USHIO INC) was employed. The TiO_2 substrates were put on temperature-controlled stages and the chamber was evacuated until the pressure became 0.1 or 10 Torr. The gap between the sample surface and the electron tube was fixed at 7 mm. Then, a shutter for EB exposure was opened and the samples were exposed to electron beam showers. The acceleration voltage and current for EB tubes were fixed at 50 kV and 100 μA/each tube, respectively. The efficiencies changed with different TiO_2 paste lots. However, when the same lot of TiO_2 pastes was employed, the results were able to be compared with each other accurately. The TiO_2 layers were immersed in N3 dye solutions in ethanol (3×10^{-3} M) at room temperature overnight. After these TiO_2 electrodes were rinsed with ethanol, they were dried at room temperature in the dark. H_2PtCl_6 solution in water was spin-coated on SnO_2/F layered glass substrates, which were heated at 450 °C to deposit Pt on the substrates. They were employed as the counter electrodes. A plastic sheet (Surlyn, Dupont. Co. Ltd)(50 μm) was inserted between a TiO_2 electrode and a counter electrode as the spacer. Electrolytes were injected in the cell at room temperature. Finally, the cells were sealed with epoxy resins. The cell area was 1 cm^2. The electrolyte contains iodine (50 mM), LiI (500 mM), *tert*-butylpyridine (580 mM) in acetonitrile. Photoelectrochemical measurements were performed using solar simulator (YSS-50A, Yamashita Denso Co. Ltd.) furnished with a xenon lamp (AM 1.5,

Table 1. Relationship between EB exposure doses and photovoltaic performances

Run	Dose $\mu C/cm^2$	Voc V	Jsc mA/cm^2	Fill factor	η %
1	0	0.73	3.50	0.64	1.64
2	16	0.72	3.20	0.64	1.48
3	160	0.71	3.98	0.62	1.75
4	1600	0.73	5.42	0.60	2.39
5	8000	0.73	7.38	0.53	2.87

Temp. on exposure: r.t., Single tube module chamber, 0.1 Torr, Photovoltaic performance: 1 cm^2 cell area, SnO_2/F- glass substrate, 30 Ω/square, AM 1.5, 100 mW/cm^2.

100 mW/cm^2).

Table 1 shows the relationship between EB exposure doses and photovoltaic performances. SnO_2/F layered glass plates were employed in this experiment. Short circuit currents (Jsc) increased with an increase in the EB exposure doses. Jsc before EB exposure was 3.5 mA/cm^2. The reference sample was treated with in the same way under vacuum without EB irradiation. The Jsc increased to 7.38 mA/cm^2 after EB exposure of 8000 $\mu C/cm^2$. Open circuit voltages did not change with the increase in the doses. Increase in the temperature of TiO_2 surfaces was negligible. These results show that TiO_2 necking proceeded even at room temperature. Figure 1 shows clearly the effectiveness for EB exposure. Table 2 shows the relation between EB exposure doses and photovoltaic performances when ITO layered plastic substrates were employed. Jsc increased after EB exposure, compared with that for the unexposed cell. Jsc had a maximum value at the EB exposure dose of 4000 μ/cm^2. This contrasts the results in the case of SnO_2/F glass substrates. The reason was not clear in this stage, but ITO may deteriorate because of the EB exposure.

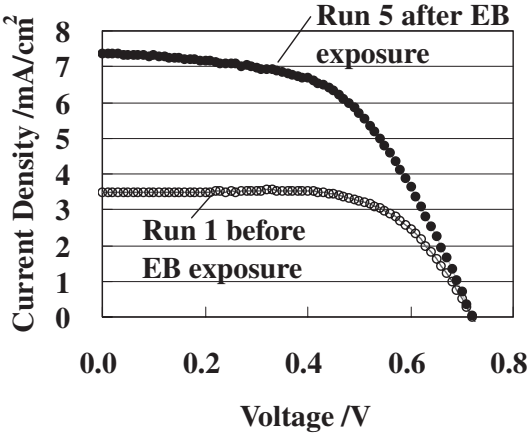

Figure 1. Current vs Voltage curves for DSSCs before and after EB exposure. Conditions: See Table 1. Cell area: 1 cm^2, AM 1.5, 100 mW/cm^2.

Table 2. Relationship between EB exposure doses and photovoltaic performances

Run	Dose $\mu C/cm^2$	Voc V	Jsc mA/cm^2	Fill factor	η %
6	2000	0.72	3.73	0.67	1.77
7	4000	0.71	4.42	0.66	2.1
8	8000	0.69	3.91	0.65	1.79
Ref	0	0.74	2.52	0.58	1.09

Temp. on exposure: 50 °C, Multitube module with 19 EB tubes, 0.1 Torr, Photovoltaic performance: 1 cm^2 cell area, ITO plastic substrate (PET), 15 Ω/square, AM 1.5, 100 mW/cm^2.

Table 3. Relation between photo-voltaic performances and temperature on EB exposure

Run	Temp °C	Voc V	Jsc mA/cm^2	Fill Factor	η %
9[a]	50	0.69	3.43	0.61	1.44
10[a]	75	0.66	3.45	0.64	1.45
11[a]	100	0.64	2.54	0.62	1.01
12[b]	50	0.68	3.72	0.63	1.60
13[b]	70	0.66	2.94	0.61	1.19
Ref	25	0.65	1.63	0.61	0.64

Temp. on exposure: 50 °C, Multitube module with 19 EB tubes, a) 0.1 Torr, b) 10 Torr, 8000 $\mu C/cm^2$, Ref: no exposure, Photovoltaic performance: 1 cm^2 cell area, SnO_2/F glass substrate, 30 Ω/square, AM1.5, 100 mW/cm^2.

Table 3 shows how the photovoltaic performance changed when substrate temperature during EB exposures increased. Decrease in Jsc was observed when the substrate temperature reached 100 °C. The same phenomenon was observed when the chamber pressure increased to 10 Torr with Ar gas. Substrate temperatures had be kept at low temperature. This implies that the Jsc increase observed in Table 1 and Figure 2 is not due to heat emitted from EB tubes. Precise reaction mechanisms are under research.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas(417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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Published on the web (Advance View) October 20, 2003; DOI 10.1246/cl.2003.1056