

Research Article

Electrochemical Deposition of Te and Se on Flat TiO₂ for Solar Cell Application

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Te and Se layers were deposited on ⟨glass/FTO/flat-TiO₂⟩ by electrochemical deposition. The Te-Se-stacked layer was annealed at 200°C, and then, the migration of Te into the Se layer by annealing was confirmed using auger electron spectroscopy (AES), which was performed by Te doping on the Se layer. Au back contact was coated by vacuum deposition on the Te-doped Se layer, resulting in superstrate-structured solar cells of ⟨glass/FTO/flat-TiO₂/Se-doped Te/Au⟩ with a 0.50 V open-circuit voltage, 6.4 mA/cm² photocurrent density, 0.36 fill factor, and 1.17% conversion efficiency.

1. Introduction

Due to the nuclear disaster in Japan (Fukushima) caused by a tsunami (on 11 March 2011), a lot of nuclear plants have been closed, which has caused big problems concerning electric power. In order to solve this energy problem, fabrication of cost-effective solar cells is urgent. At present, the price of silicon solar cells has become more affordable (58.5 euro cents/W module) [1], but the cost decline has not been enough to provide an alternative to nuclear generation systems, with the final goal being 0.5 dollar/W [2]. Three aspects necessary to reduce the cost of solar cell fabrication are

- (1) to omit expensive materials (In),
- (2) to set the simple production line without vacuum processing,
- (3) to omit toxic materials (e.g., H₂Se, H₂S, and Cd).

In order to fabricate such cost-effective solar cells, organic and dye-sensitized solar cells have been investigated, as printed solar cells [3–5]. However, because of the organic dyes, the stability of solar cells has been obscure. A TiO₂/Se solar cell is promising as a cost-effective In-Ag-free solar cell, which was fabricated using the vacuum deposition method

with Te doping on the Se layer [6]. In this study, selenium and tellurium were electrochemically deposited onto flat TiO₂ layers, resulting in the simple superstrate structure and simple process solar cells. We have optimized the heat treatment for Te doping into the Se layer. The solar cells did not include expensive materials (indium), toxic materials (cadmium and mercury), or expensive processes such as CVD and sputtering, providing a cost-effective solar system.

2. Experiment

Transparent conducting oxides of fluorine-doped tin-oxide-(FTO-) coated glass plates (Nippon Sheet Glass TEC-7, $t = 2.2$ mm) were used as substrates. Figure 1 shows the fabrication processes of ⟨glass/FTO/TiO₂/Te-doped Se/Au⟩. First, TiO₂ layers ($t = 100$ nm) were coated onto ⟨glass/FTO⟩ substrates by spray pyrolysis deposition (SPD) at 400°C. The solution for spraying the TiO₂ compact layer was a mixture of titanium acetylacetonate (TAA) and ethanol with an ethanol/TAA volume ratio of 9 : 1. The TAA was prepared by slow injection of acetylacetonate (99.5% pure; Kanto Chemical Co.) into titanium tetraisopropoxide (97% purity; Kanto Chemical Co.) with a mole ratio of 2 : 1.

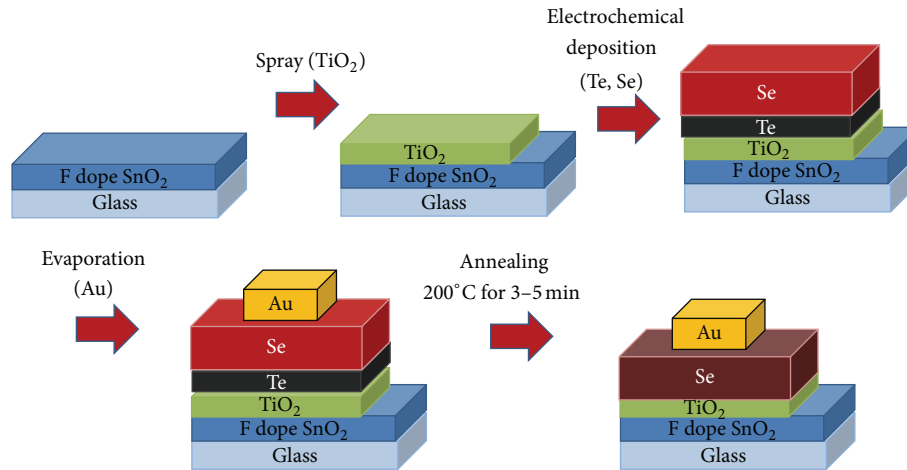


FIGURE 1: Fabrication scheme of electrodeposited Se-Te solar cells.

An electrochemical deposition (ECD) method of selenium has been reported by Chraïbi et al. [7]. For the ECD of Te and Se on the TiO_2 layer, the reported method has been modified in this paper, as shown below. The ECD solution for tellurium deposition included 0.1 M NaOH (Kanto Chemical Co., Inc.) and 10 mM TeO_2 (Wako Pure Chemical Industries, Ltd.) dissolved in water, and then HCl (20 w/w% concentration; Kishida Chemical Co., Ltd.) was added to make $\text{pH} = 2.1$. Tellurium layers were coated by the ECD method at -0.7 V (versus Ag/AgCl, BAS Inc.). Details concerning the tellurium deposition duration are shown in Section 3.

The solution for selenium ECD included 0.3 M NaCl (99.5% pure; Kanto Chemical Co., Inc.), and 10 mM H_2SeO_3 (97% pure; Kanto Chemical Co., Inc.) dissolved in water, and HCl (20 w/w% concentration; Kishida Chemical Co., Ltd.) was added to make $\text{pH} = 2.1$. Selenium absorber layers were deposited for 10 min at -0.7 V and -1.0 V (versus Ag/AgCl) on FTO and TiO_2 by ECD, respectively. The thickness of the Se layer was ca. 100 nm, confirmed by scanning electron micrograph.

The selenium solar cells were completed with gold electrodes deposited as a back contact by an evaporation method. After the back contact deposition, all samples were annealed in the air at 200°C for 3 min to improve the crystallinity of the selenium layers. The area of cells for the photocurrent density-voltage (J - V) measurement was 0.25 cm^2 .

Photovoltaic characteristics were measured by an AM 1.5 solar simulator equipped with a xenon lamp (YSS-100A, Yamashita Denso, Japan). The power of the simulated light was calibrated to 100 mW cm^{-2} using a reference Si photodiode (Bunkou Keiki, Japan). I - V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a DC voltage current source (6240, ADCMT, Japan). For the analysis of electrochemically deposited Se layers, auger electron spectroscopy (AES) was measured (JAMP-9500F, JEOL). Absorption spectra were

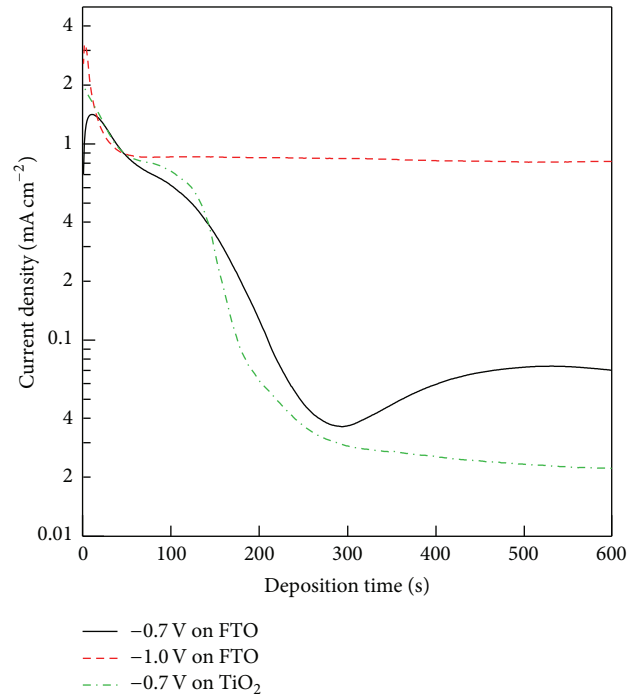


FIGURE 2: Time-electrodeposition current curves at the selenium electrodeposition at -0.7 V and -1.0 V (versus Ag/AgCl) using FTO electrodes and at -0.7 V (versus Ag/AgCl) using TiO_2 electrode.

measured by an ultraviolet-visible spectroscopy (Lambda 750 UV/VIS Spectrometer, Perkin-Elmer).

3. Results and Discussion

Figure 2 shows the variation of currents in selenium deposition with different voltages (-0.7 V and -1.0 V versus Ag/AgCl) and different electrodes (FTO and TiO_2). When a large voltage (-1.0 V versus Ag/AgCl) was applied, a high

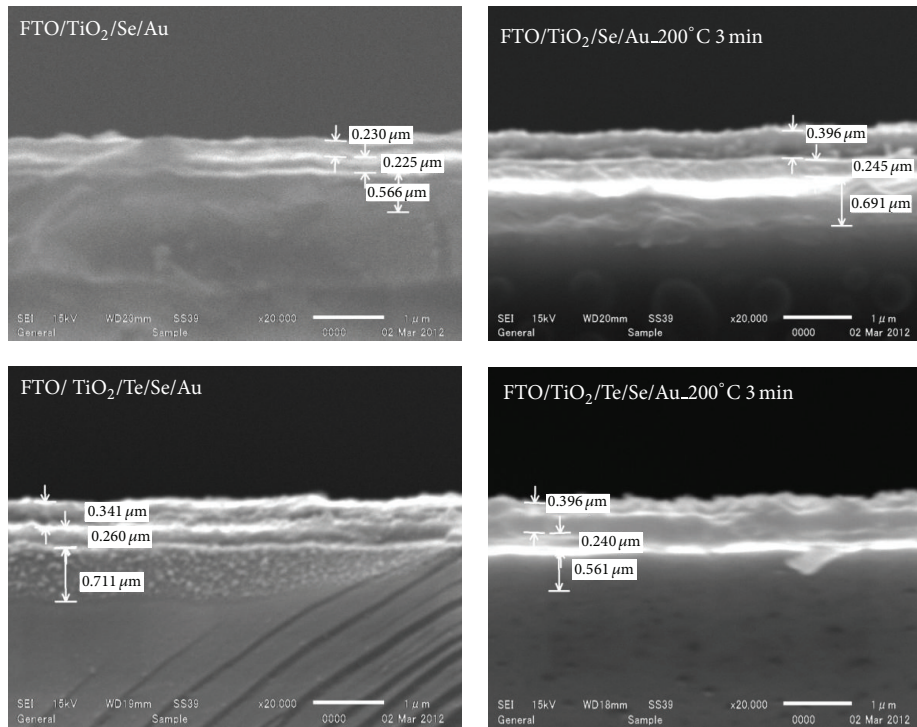


FIGURE 3: SEM pictures of the cross-sections of selenium-deposited electrodes with and without tellurium and before and after annealing at 200°C for 3 min.

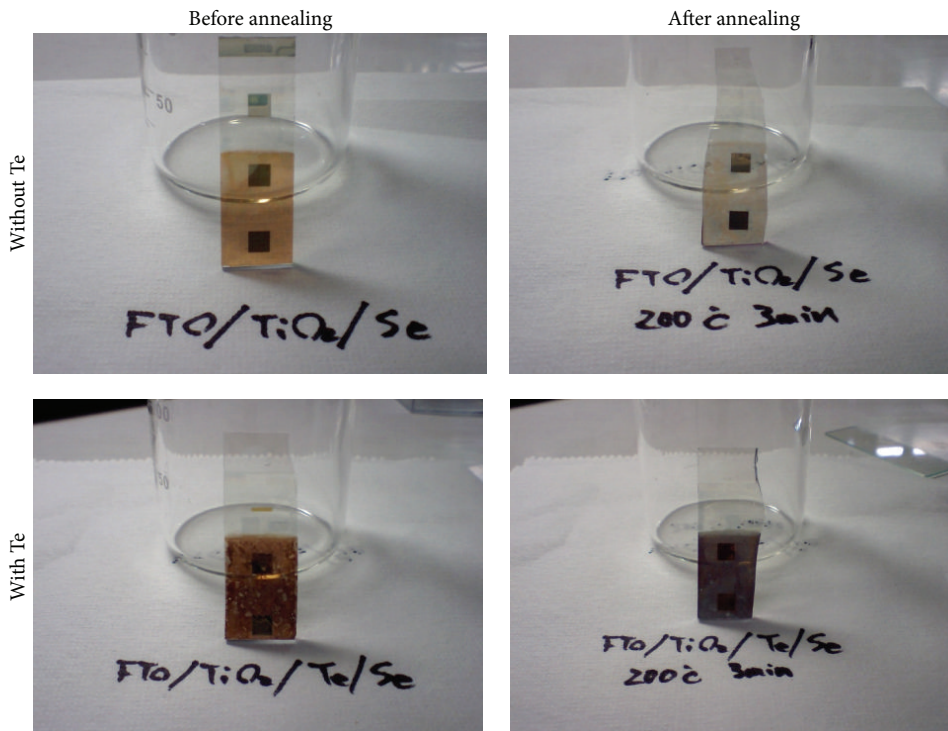


FIGURE 4: Photographs of selenium-deposited electrodes with and without tellurium and before and after annealing at 200°C for 3 min.

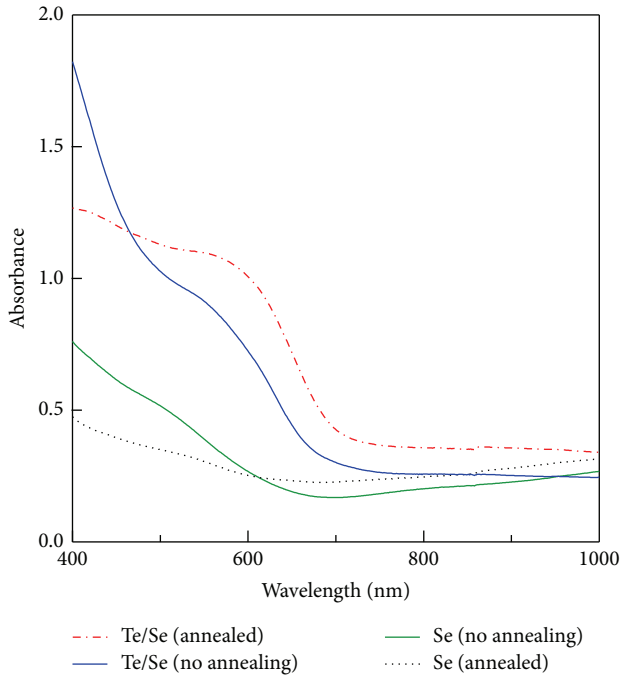


FIGURE 5: Absorption spectra of electrodeposited Se (with/without Te) layers on glass/FTO/TiO₂ substrates with and without annealing at 200°C for 3 min.

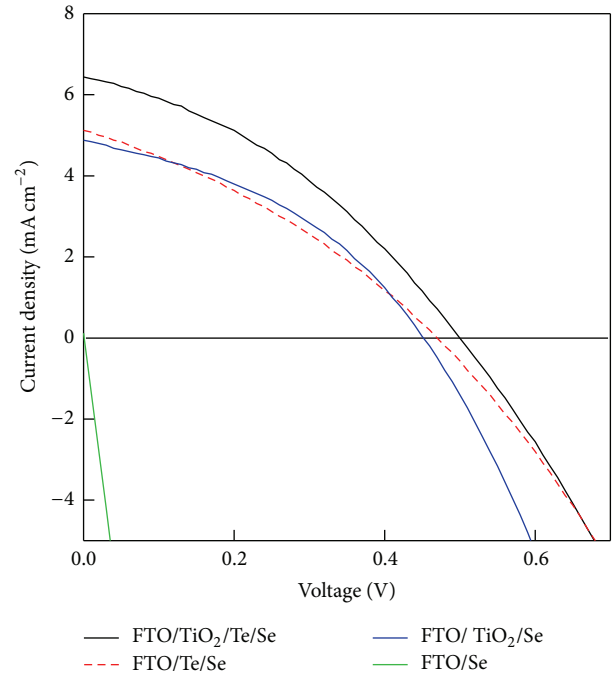


FIGURE 7: Photocurrent-voltage curves of electrochemically deposited selenium solar cells. Each cell size was 25 mm².

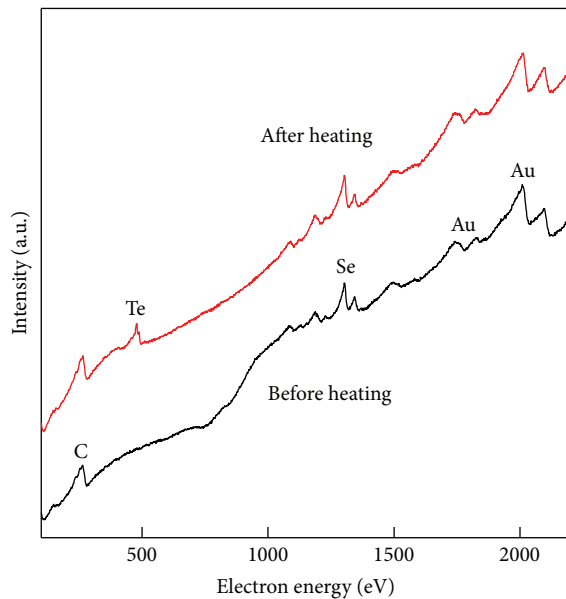


FIGURE 6: AES spectra of electrodeposited Te/Se stacked layers before and after annealing.

constant current density of 1 mA cm^{-2} was observed. However, the resulting selenium layers were too inhomogeneous to form solar cells. Therefore, a small voltage (-0.7 V versus Ag/AgCl) was applied to the selenium deposition for solar cell utilization. Although the deposition current decreased to less than 0.1 mA cm^{-2} due to the high resistivity of

the selenium layer, the resulting selenium layers became relatively homogeneous for the fabrication of solar cells.

The cross-sections of electrochemical-deposited selenium layers on TiO₂ were observed using SEM (Figure 3). The selenium before annealing and the TiO₂ layers were $0.2\text{--}0.4 \mu\text{m}$ and $0.22\text{--}0.26 \mu\text{m}$, respectively. Although the TiO₂ thickness was highly reproducible due to the spray pyrolysis deposition, the electrochemical-deposited selenium thickness was valuable in each deposition. However, the selenium layers were smooth enough for solar cell application. The tellurium layer was not observable because it was too thin for SEM observation. After annealing, the remaining of the selenium layer was confirmed.

Figure 4 shows images of selenium electrodes with and without tellurium, as well as before and after annealing. In selenium electrodes without tellurium, the annealing diminished the selenium's color. The reason is not clear, but selenium can be deposited effectively on tellurium layer. Moreover, the tellurium maintained the selenium's color during the annealing.

Figure 5 shows absorption spectra of electrochemically deposited selenium layers on (glass/FTO/TiO₂) substrates. The pure selenium layer before annealing showed absorption below the 650 nm wavelength and contained a red color. After annealing at 200°C for 3 min, the absorbance decreased and the layer becomes more transparent. These results correspond to the images in Figure 4. Since the layer can be observed in the cross-section (Figure 3), selenium may be able to be oxidized in the heating treatment.

On the other hand, with a small addition of tellurium (by ECD for 30 seconds) between TiO₂ and selenium, the

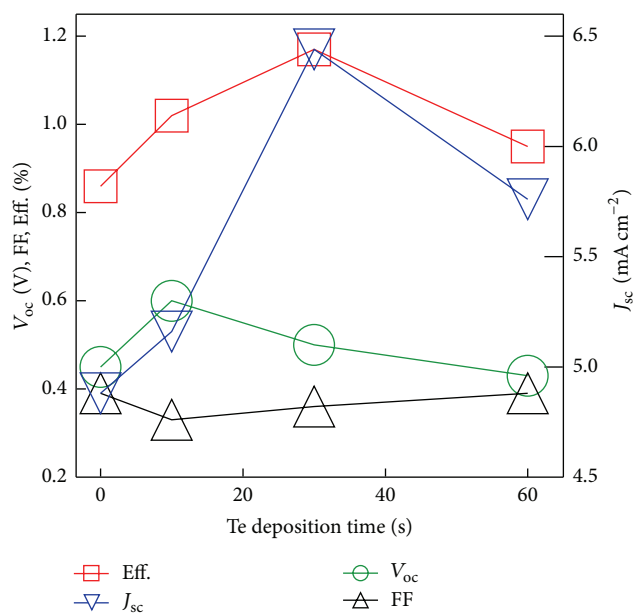


FIGURE 8: Variations of photovoltaic characteristics with duration of tellurium electrochemical deposition: open-circuit photovoltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factors (FF), and photoenergy conversion efficiency (η).

absorbance was improved compared to the pure selenium layer. Moreover, after heating, the absorbance was improved and the absorbance edge was shifted to a longer wavelength. The color was nearly black, which suggested photo absorbance of the whole visible light spectrum. At least, the selenium evaporation was suppressed by the thin tellurium layer. The enlargement of the selenium crystal may improve absorbance by annealing.

Figure 6 shows the auger electron spectroscopy (AES) results of tellurium/selenium-stacked layers before and after annealing. AES was measured from the Se layer surface. Hence, the tellurium layer was covered by the selenium layer, and the tellurium peak was not observed. On the other hand, after annealing, the tellurium peak was observed by the selenium surface measurement. Therefore, the tellurium was migrated in the selenium layer from the bottom to the surface, resulting in tellurium doping on the selenium.

Figure 7 shows photocurrent voltage curves of selenium solar cells. At first, the (glass/FTO/Se/Au) cell showed no significant photovoltaic effect. After tellurium doping on the selenium layer, a photovoltaic effect emerged. On the other hand, without tellurium doping, the TiO_2 layer also improved the photovoltaic effects of the selenium solar cells. The photovoltaic improvement by TiO_2 was comparable to tellurium doping. Both the short-circuit photocurrent density (J_{sc}) and the conversion efficiency were improved by simultaneously applying TiO_2 and tellurium to selenium cells, creating (glass/FTO/ TiO_2 /Te-doping Se/Au) cells.

Tellurium effects on photovoltaic characteristics were summarized in Figure 8. The highest efficiency of the selenium solar cells was obtained at 30 sec electrochemical deposition of tellurium on (glass/FTO/ TiO_2) substrates. However,

the excess of tellurium addition deteriorated J_{sc} and open-circuit photovoltage (V_{oc}), resulting in the deterioration of the conversion efficiency (η). The thickness of the tellurium layer was very thin and could not be observed by SEM.

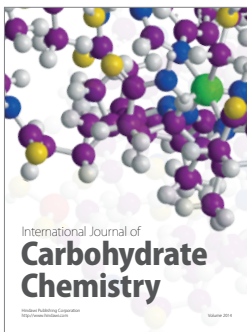
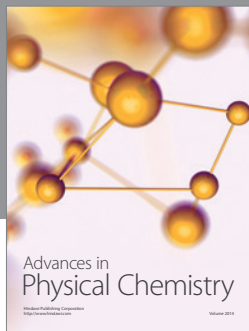
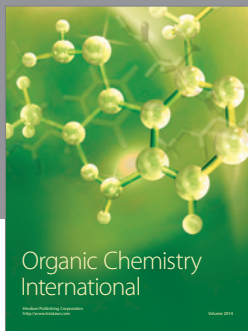
In conclusion, selenium solar cells were prepared by electrochemical deposition. Te doping and TiO_2 improved the photovoltaic characteristics. The simultaneous utilization of Te doping and TiO_2 performed the best results. Although the electrochemical deposited-Te/Se layers produced only a 1.17% conversion efficiency, this electrochemical deposition method can be applied to other systems such as DSC, CIGS, or OPV to create nonvacuum processed solar cells. We have tried to improve the conversion efficiency using a porous TiO_2 layer such as dye-sensitized solar cells [8]. Without Te addition to the Se layer, the conversion efficiency was raised to 3.0% on porous TiO_2 electrodes. However, the conversion efficiency with Te addition through a porous TiO_2 layer deteriorated the conversion efficiencies (data not shown). If we can find the reason why Te addition could not improve the photovoltaic effect using the porous TiO_2 layer, we may create a new solar cells such as (porous TiO_2 /Te/Se) cells. Hence, we believe that this report can contribute to the creation of cost-effective solar cells.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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