

Article

Effect of Surface Treatment by Chemical-Mechanical Polishing for Transparent Electrode of Perovskite Solar Cells

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Abstract: Perovskite solar cells (PSCs) are usually fabricated by using the spin coating method. During the fabrication process, the surface status is very important for energy conversion between layers coated in the substrate. PSCs have multilayer-stacked structures, such as the transparent electrode layer, the perovskite layer, and a metal electrode. The efficiency and uniformity of all layers depend on the surface status of the transparent electrode coated on the glass substrate. Until now, etching methods by chemical processes have been introduced to make the substrate surface smooth and uniform by decreasing surface roughness. However, highly reactive chemical treatments can be harmful to the environment. In this study, we employed an eco-friendly chemical-mechanical polishing (CMP) process to ensure the fluorine-doped tin oxide (FTO) substrate is treated with a smooth surface. Before the perovskite layer and electron transport layer (ETL) are applied, the TiO_2 layer is coated with the FTO substrate, and the surface of the FTO substrate is polished using CMP. As a result, the CMP-treated surface of the FTO substrate showed a smooth surface, and the PSCs with CMP treatment did not require conventional TiCl_4 treatment.

Keywords: perovskite; solar cell; CMP; surface; FTO

1. Introduction

This research focuses on solar energy as the most sustainable energy due to its clean, abundant, and unlimited energy source. Compared to silicon-based solar cells, perovskite solar cells (PSCs) based on organic–inorganic hybrid materials have been introduced to next-generation solar cells, with low-cost production, light weight, and flexible device applications [1–4]. These types of organic–inorganic-materials-based solar cells are usually fabricated by using the spin coating method. In their fabrication process, the smoothness of the surface between the transparent electrode (fluorine-doped tin oxide, FTO) and the organic layers is needed to uniformly and widely cover the films on the substrate [5–7].

Until now, etching methods by chemical processes have been introduced by many research groups to make substrate surfaces smooth and uniform. After the introduction of a surface treatment using TiCl_4 , many groups started to use the treatment as the standard procedure for fabricating PSCs [8–10]. Even though it is a well-established process to improve the surface, the TiCl_4 treatment process has disadvantages, such as its remaining residue after surface treatment, difficulties in the control of etching rate, toxicity, and pollution problems. TiCl_4 can be very dangerous due to its high reactivity with oxygen and water [11–13]. However, the surface status of the FTO substrate still remains rough, and this has effects on the layers stacked on the spin-coating process.

To have a smooth surface without problems, we propose the direct treatment of the FTO/glass surface using the chemical-mechanical polishing (CMP) method. The CMP method could provide the

ability to control the roughness in the range of a nanometer, and it is a very simple process (rotation machine, pad, and the slurry solution containing powder with more hardness, stronger than that of the film to be treated), compared to the typical surface treatment using strong oxidation chemicals [14,15].

More importantly, the method is relatively more eco-friendly than most chemical treatment methods. The chemicals in this CMP method are not that impactful to the environment. Since this method is more pro-environmental than other chemically reactive treatments, it can reduce the adverse effects on the environment during the mass production of solar cells. Due to these merits, the manufacturing industry of semiconductor production processes, such as integrated circuits (IC) and electronic devices, have been using CMP for decades [16–18]. Moreover, CMP-related study has not been reported in PSC fields yet.

In this study, we used the CMP method to treat the surface of perovskite solar cells (PSCs). We created a chemical-mechanical polished FTO substrate, then the PSC layer was coated onto the FTO substrate. The surface of the FTO substrate was smoothed by the chemical mechanical polishing (CMP) process, as compared to the TiCl_4 treatment. We investigated the effects of the status of the substrate surface on the fabrication process without using the conventional chemical treatment method.

2. Experiment Details

2.1. Surface Treatment

FTO glass (thickness < 2.2 mm, sheet resistance < 8 ohm/sq) was purchased from Wooyang GMS Company. Al_2O_3 powder (model: 90-1870858, average particle size: 0.3 μm) and polishing pad (model: 180-10050, diameter = 200 mm) were purchased from Chinwoo Tech. Company and used without further processing.

The slurry solution was prepared in the laboratory through the following process. Firstly, we dissolved TiO_2 powder in deionized water (< 18 ohm) and treated it by ultrasonication for 10 min. Before treating the surface of the substrate, we allowed water to flow through a polishing pad by rotating its table for 5 min without a slurry solution. As the slurry solution dropped at a rate of 1 mL/sec on one side of the polishing pad, the FTO substrate was put down on the opposite side, and was pressed with 0.0005 g/mm^2 of pressure. After completing the CMP process, samples were ultrasonicated by the conventional cleaning process (acetone, ethanol, and DI water). In Figure 1, we show the schematics diagram and surface treatment process chart of the chemical mechanical polishing (CMP) process.

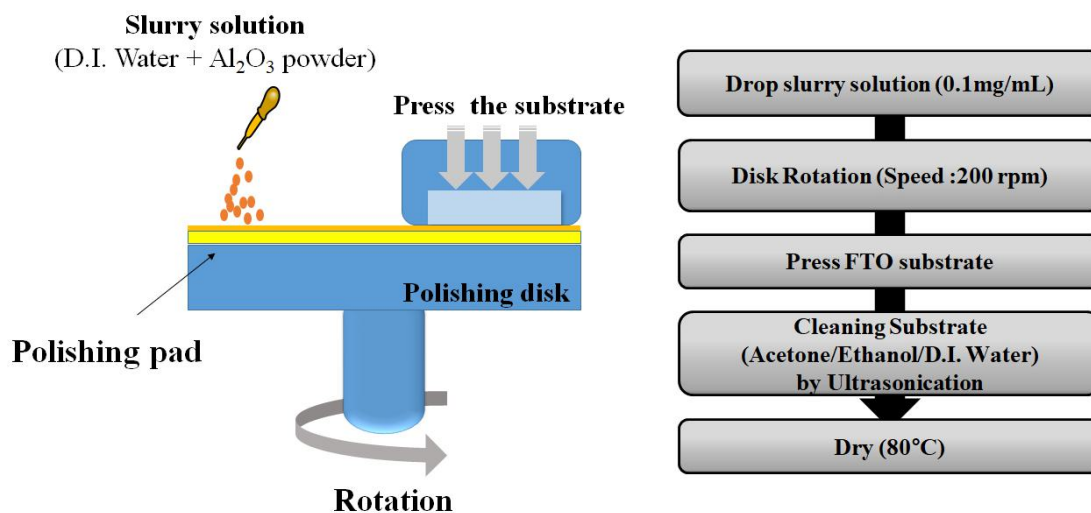


Figure 1. Schematics diagram and surface treatment process chart of the chemical mechanical polishing (CMP) process.

2.2. Fabrication of Perovskite Solar Cells

We purchased all chemical materials from Sigma-Aldrich Chemical Company and used them without further purification. To make perovskite solar cells, we used a two-step spin-coating procedure to form $\text{CH}_3\text{NH}_3\text{PbI}_3$ [19,20]. A lab-made TiO_2 paste was used for the mesoporous and compact TiO_2 layer on the FTO substrate. After the PbI_2 solution was spin-coated on the mesoporous TiO_2 layer, a $\text{CH}_3\text{NH}_3\text{I}$ (MAI) solution in 2-propanol was loaded on the PbI_2 -coated substrate. Then, the Spiro-MeOTAD was spin-coated on the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer. The metal electrode (Au) was deposited by the thermal evaporator.

2.3. Measurements

The surface morphology was measured by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) and scanning probe microscopy (SPM, Park Systems XE-150). The crystallographic structural properties of the samples were measured by X-ray diffraction (XRD, Rigaku RINT2100) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$, 40 kV, 40 mA) with 2-theta scan mode. The conversion efficiency properties of the fabricated cells were measured using a current–voltage (J–V) solar simulator (McScience Company K3400) at AM 1.5 G (100 mW/cm^2). Electrical properties of the films were examined by a four-point probe and Hall-effect measurement (HMS-3000, Ecopia).

3. Results and Discussion

To observe the property variations of surface treatment by chemical-mechanical polishing, we investigated the optical, structural, and morphological properties of the samples. Figure 2 shows the optical transmittance of the FTO substrate by the CMP surface treatment time.

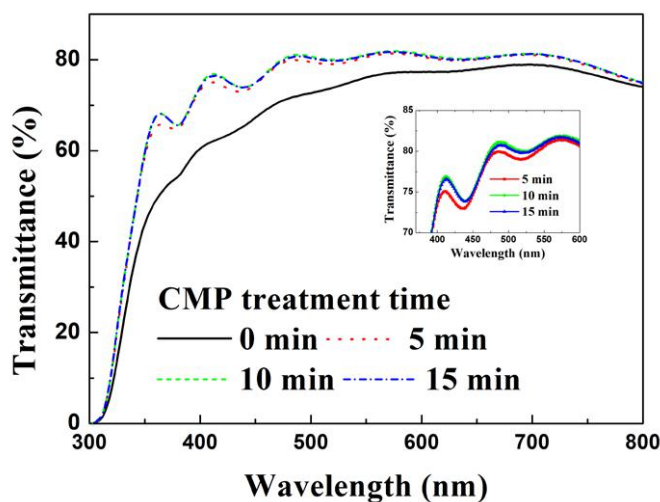


Figure 2. Optical transmittances of the fluorine-doped tin oxide (FTO) substrate as a function of CMP surface treatment time.

After treating their surface, the transmittance of the FTO substrate increases more than the untreated surface, as shown in Figure 2. The increase of optical transmittance is thought to have been caused by the status of the surface of the FTO film. The transmittance of under 72% in the range of 400–500 nm for the sample dramatically increased, to over 82%, following the CMP process. The sample dramatically increased, to over 87.3%, following the CMP process. As CMP treatment time increased, the roughness of the FTO film surface became smoother without dispersion and scattering of light.

Improving the transmittance of the substrate contributed to enhancing the efficiency of the solar cell which collects light through the transparent substrate [21,22]. Meanwhile, their light transmittance

did not show a consistent trend in dependence on CMP surface treatment time. After treating the substrate for 15 min, the optical transmittance decreased below that of 10 min, as shown in the insert in Figure 2. That phenomenon was thought to be attributed to some variation of the FTO substrate due to the longer treatment time.

We investigated the effect of crystal structure on the effect of CMP treatment. Figure 3, which is observed in the XRD patterns of the FTO substrate, could be understood as the variation in crystallinity before and after CMP treatment (0–15 min). All XRD peaks of the sample were detected in the range of 10–80° 2theta. All strong diffraction peaks of samples matched with the standard FTO peaks. Any structural shifts and changes were not observed from XRD, neither before nor after CMP treatment. In addition, this confirmed that the CMP method did not caused any secondary peaks from residue. This means that in the CMP process, both chemical and mechanical actions between the substrate and slurry solution are completely removed. We could not observe any evidence of structural deformation in the FTO substrate.

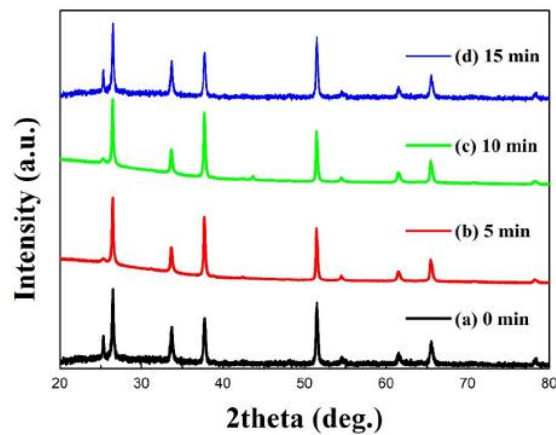


Figure 3. XRD patterns of the FTO substrate before and after the CMP process.

We observed the morphology of samples before and after the CMP process. As you can see in Figure 4, the film thickness of the FTO is approximately 500 nm. Before CMP, the as-prepared FTO surface is not uniform, and is very rough. After CMP treatment, the surface of the FTO substrate changed to a smooth and uniform surface, and the bumps observed in the FTO surface before CMP were not detectable, as shown in Figure 4a–h.

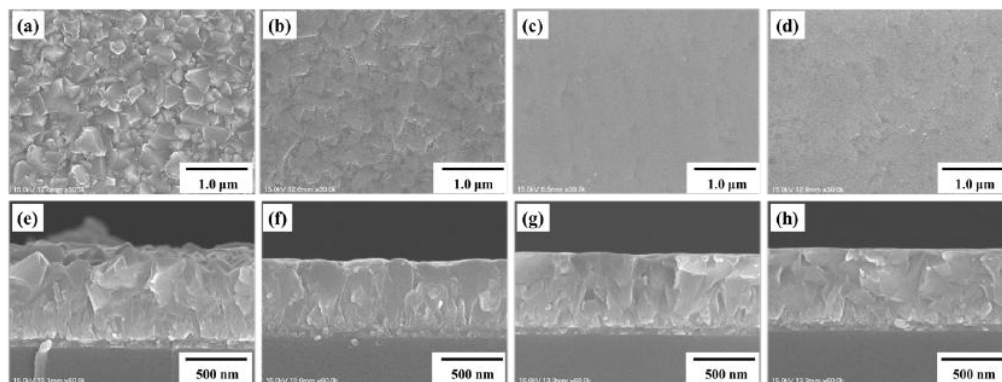


Figure 4. Surface and cross-sections of FE-SEM images of the FTO substrate before and after the chemical mechanical polishing (CMP) process. Before CMP: (a) and (e); CMP treatment 5 min: (b) and (f); CMP treatment 10 min: (c) and (g); and CMP treatment 15 min: (d) and (h).

We measured the sheet resistance of the FTO substrates with and without CMP treatment by using four-point probe equipment. As shown in Figure 5, the sheet resistance of all samples increased. After CMP treatment, sheet resistance increased by 5%.

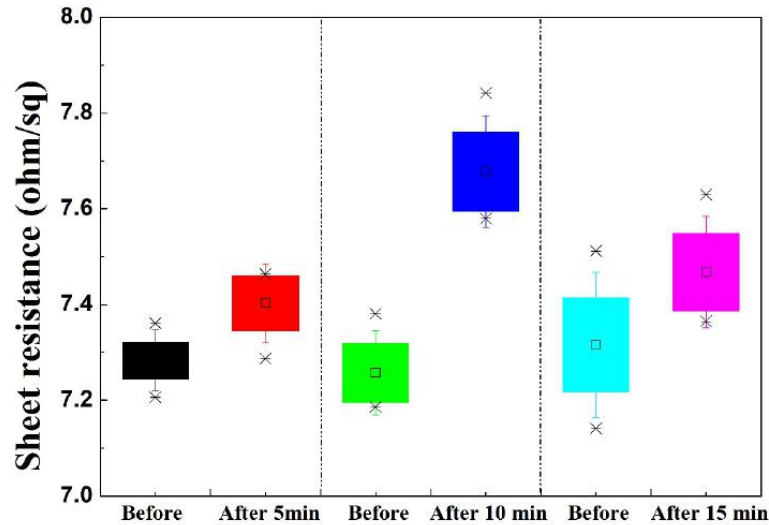


Figure 5. Sheet resistance of the FTO substrate with and without CMP treatment. (They have minimum values, maximum values, and median values that are displayed at the middle line in each box.).

Measurement made using the Hall-effect, as well as more detailed electrical properties of samples, are shown in Figure 6. Without surface treatment, commercial FTO substrate had approximately 7–8 ohm/sq of sheet resistance. It is well known that sheet resistance is strongly connected with mobility and carrier concentration. The higher sheet resistance was thought to lower carrier concentration. Carrier concentration would be attributed to oxygen vacancies, such as the main carriers in films based on an oxide complex [23,24]. The oxygen vacancies would be lower due to the chemical reactions with the slurry in the CMP process. On the other hand, their mobility indicated the opposite trend.

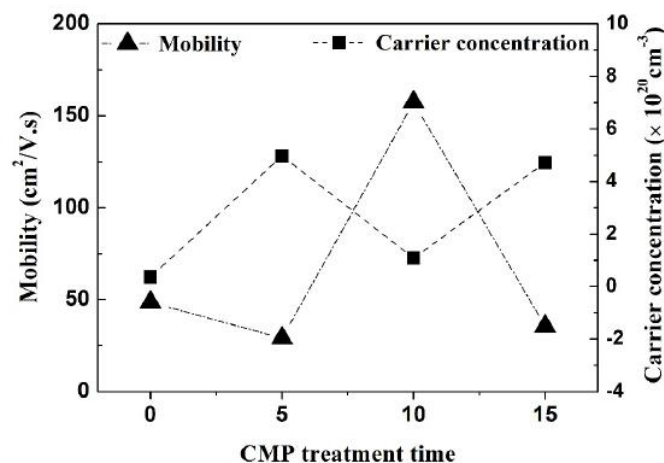


Figure 6. Electrical properties of the FTO substrate as a function of CMP surface treatment time.

Among the three samples, the sample with 10 min of treatment time has the best electrical properties under various conditions. We selected the FTO substrate treated for 10 min in the CMP process and a more detailed surface morphology was checked.

The roughness of each surface was observed using AFM, as shown in Figure 7. More detailed values of surface roughness are shown in Table 1. The surface roughness (RMS) of the FTO substrate after CMP treatment decreased from 32.996 to 11.777 nm in Figure 7a,b. Their R_a (roughness average) value also decreased from 26.620 to 9.132 nm ($RMS = 15.317$ nm). From the AFM and FE-SEM results, we confirmed that CMP treatment effectively smoothed the surface of the FTO substrate. The results indicate that the surface roughness was greatly improved in the nano region, and the removal of large peaks was observed in the FE-SEM (Figure 4).

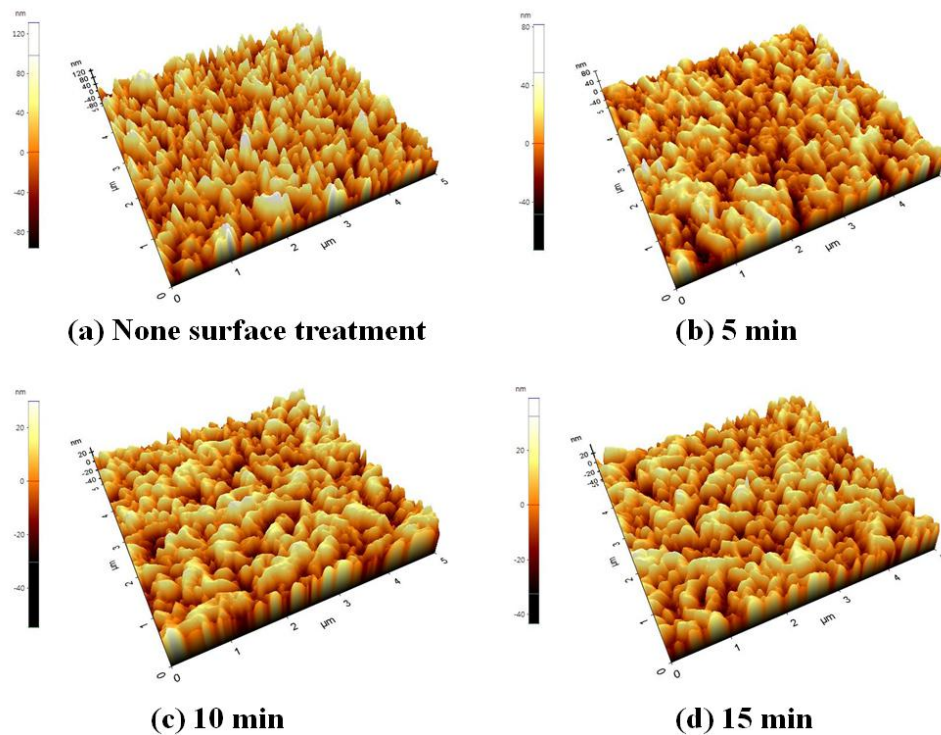


Figure 7. Surface morphology of the FTO substrate with and without the CMP process. (a) None surface treatment, (b) 5 min, (c) 10 min, (d) 15min.

Table 1. Surface roughness parameters of the surface-treated FTO substrate.

	Treatment Time	R_a (nm)	RMS (nm)
None surface treatment	-	26.620	32.996
After CMP treatment	5 min	12.917	16.043
	10 min	9.320	11.379
	15 min	9.132	11.177

R_a = Roughness Average, RMS = Root Mean Square.

As a result, we confirmed that the CMP process is highly effective in the improvement of the surface of the substrate without changing its structure. As is commonly observed in the CMP process of semiconductor devices, the processing time of CMP can present different performances of PSCs. To check the effect of treatment time of CMP in PSC, we prepared PSCs with a series of processing times (0–15 min) with the surface treatment, and the effect of the CMP process on PSCs was investigated. We prepared four of the bare samples without CMP treatment and 18 CMP-treated samples (5, 10, and 15 min), and their photovoltaic performance was investigated in the solar-simulator under AM 1.5 G illumination (100 mW/cm^2).

The photovoltaic performance results of the prepared samples are shown in Figure 8. The details of the device parameter values recorded from the solar simulator are listed in Table 2. All calculated values in Figure 8 and Table 2 are averaged values.

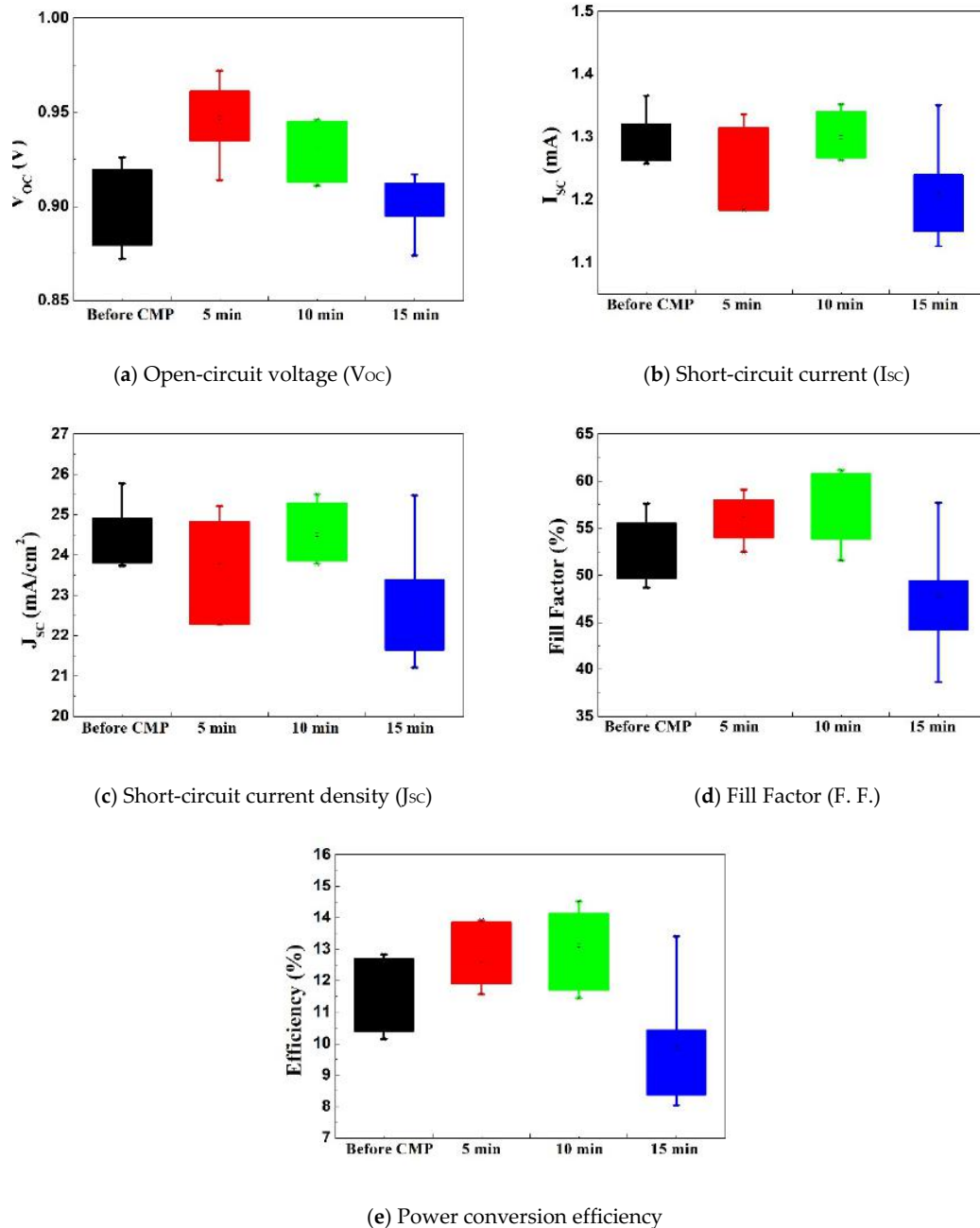


Figure 8. Photovoltaic properties of perovskite solar cells before and after CMP surface treatment; (a) open-circuit voltage, (b) short-circuit current, (c) short-circuit current density, (d) fill factor, and (e) power conversion efficiency of the prepared perovskite solar cells (PSCs) device. The box plots of (a)–(e) were drawn vertically indicating the data distribution of photovoltaic parameters recorded from the solar simulator. They have minimum values, maximum values, and average values that are displayed at the middle line in each box.

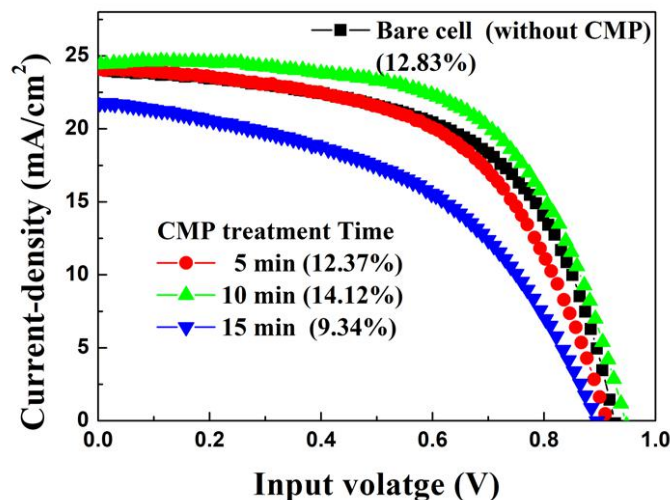
Table 2. Photovoltaic performance parameters (J_{SC} , V_{OC} and Fill Factor, and PCE).

		V_{OC} ^a (V)	I_{SC} ^b (mA)	J_{SC} ^c (mA/cm ²)	F. F. ^d (%)	PCE ^e (%)
Bare cell (Before CMP)		0.899	1.291	24.365	52.582	11.551
		(0.024)	(0.050)	(0.947)	(3.879)	(1.351)
	5 min	0.947	1.264	23.833	56.005	12.648
		(0.020)	(0.065)	(1.256)	(2.476)	(0.999)
	10 min	0.931	1.306	24.621	58.270	13.387
		(0.015)	(0.033)	(0.657)	(3.081)	(1.173)
After CMP treatment	15 min	0.901	1.206	22.742	47.751	9.840
		(0.015)	(0.082)	(6.269)	(6.269)	(1.939)

^a Open-circuit voltage, ^b short-circuit current, ^c short-circuit current density, ^d fill factor, and ^e power conversion efficiency. () = (Standard Deviation).

The PSCs without the CMP process (Bare cell) had a J_{SC} of 24.365 mA/cm², F.F. of 52.582%, V_{OC} of 0.899 V, and an efficiency of 11.551%. As the CMP process time increased, the average power conversion efficiency of the samples with CMP treatment increased from 12.648% to 13.387%. After surface treatment, J_{SC} also slightly decreased due to increasing sheet resistance of the FTO film. Moreover, the series resistance also increased, and that means that the elements of the high bandgap interfered with the movement of electrons, and the movement distance of electrons increased.

It was discovered that increasing treatment time, due by enhancing mobility, improved surface roughness of the samples. Considering the increase of its efficiency, it can be confirmed that increasing mobility is effective in increasing efficiency, as the recombination of electrons and holes is lowered [25]. However, PSCs with 15 min of the CMP process decreased to an average 9.840% of power conversion efficiency, which shows smaller efficiency than the bare cell (12.648%). We believe that a longer duration of CMP treatment can orchestrate the degradation of FTO properties due to the surface damage. With optimal processing conditions, the surface of the FTO substrate is transformed to be uniform and smoother, since the nature of conduction is still well-maintained. However, we observed that the mobility of FTO glass after 15 min of CMP treatment increased from 48.49 (Bare cell) to 35.49 ohm/sq, as shown in Figure 9.

**Figure 9.** Current density of perovskite solar cells as a function of CMP treatment time.

We selected the best cells in the PSC samples prepared at each fabrication condition and constructed the current-density curve of fabricated cells as a function of CMP process time in Figure 9.

Compared to the bare cell, the efficiency of PSCs prepared with a smooth FTO substrate treated by CMP processes improves by 10% (from 12.83% to 14.12%). It was confirmed that the smooth surface in the current in relation to the graph in Figure 9 can be attributed to the scattering and absorbance of light, enhancing the photovoltaic performance of the perovskite solar cells [26].

4. Conclusions

In this study, we investigated the effect of the CMP process on the fabrication of PCSs. The surface of the FTO substrate was treated to become uniform and smooth through the CMP treatment. All chemical materials related to the energy conversion of solar cells were prepared on the surface-treated FTO substrate. At the simulated solar irradiation power density of 100 mW/cm² (AM 1.5 G), and after polishing the surface of the FTO substrate by CMP equipment (Time: 10 min), the FTO substrate had a smooth surface compared to FTO films without polishing. The RMS 27.825 nm (Ra = 21.89 nm) decreased to 15.317 nm (Ra = 12.352 nm). Despite changing the surface morphology, PSCs with and without the polishing process have efficiencies of 14.12% and 12.37%, respectively. However, after a polishing time of 15 min, the efficiency decreased to 9.34%.

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Conflicts of Interest: The authors declare no conflict of interest.

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