

Research Article

Improve the Properties of p-i-n α -Si:H Thin-Film Solar Cells Using the Diluted Hydrochloric Acid-Etched GZO Thin Films

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Gallium-doped zinc oxide (GZO) thin films were deposited on glass, and the process parameters are RF power of 50 W and working pressure of 5 mTorr, and the substrate temperature was changed from room temperature to 300°C. At first, the thickness was around 300 nm by controlling the deposition time. The effects of substrate temperature on the crystallinity, lattice constant (c), carrier mobility, carrier concentration, resistivity, and optical transmission rate of the GZO thin films were studied. The 200°C-deposited GZO thin films had the best crystallinity, the larger carrier concentration and carrier mobility, and the lowest resistivity. For that, the thickness of the GZO thin films was extended to around 1000 nm. Hydrochloric (HCl) acid solutions with different concentrations (0.1%, 0.2%, and 0.5%) were used to etch the surfaces of the GZO thin films, which were then used as the substrate electrodes to fabricate the p-i-n α -Si:H thin-film solar cells. The haze ratio of the GZO thin films increased with increasing HCl concentration, and that would effectively enhance light trapping inside the absorber material of solar cells and then improve the efficiency of the fabricated thin-film solar cells.

1. Introduction

Transparent conducting oxides (TCOs) are electrical conductive materials with a comparably low absorption of light. They are usually prepared with thin film technologies and widely used in the applications of the various optoelectrical devices such as solar cells, flat panel displays (FPDs), optoelectrical interfaces, and circuitries [1]. The TCOs also show a good combination of electrical conductivity at ambient temperature and optical transparency in a visible region. Thus, as n-type TCOs are of special importance for thin film solar cell production, indium-tin oxide (ITO) [2] and the reasonably priced aluminum-doped zinc oxide (ZnO:Al) thin films [3] are discussed with view on preparation, characterization, and special occurrences. ITO thin films exhibit disadvantages including toxicity, instability of hydrogen plasma, and increasing price due to the global indium

shortage. Accordingly indium-free TCO thin-film materials have attracted considerable attention. Although the Al-doped ZnO thin films present favorable electrical properties, aluminum exhibits significantly high reactivity to oxygen, which will lead to the oxidation during film growth and then result in the degradation of electrical properties. Because the gallium is less reactive to oxidation, Ga-doped ZnO (GZO) TCO materials have been reported to have better stability [4, 5].

In the past, many methods were investigated to improve the efficiency of the α -Si:H thin-film solar cells. Ferry et al. utilized nanoimprint lithography to pattern the back contact of an n-i-p α -Si:H solar cell, and the optimized shape of the nanopatterned back reflector could improve the absorption of red part of the spectrum (600–800 nm) [6]. Lare et al. printed periodic Ag nanoparticle arrays onto a completed thin-film

α -Si:H solar cell, which formed a effective mode coupling to decrease light scattering and enhance the photocurrent [7]. Rough interfaces are usually introduced into solar cells by using substrates with textured surface [8]. For solar cells in a superstrate configuration, a glass plate covered with textured transparent conductive oxide (TCO) film is usually used. The TCO layer forms the front contact of the superstrate solar cells and has to exhibit good electrical (high conductivity) and optical (high transmittance) properties. Because a suitable textured surface is very important to scatter an incident light, particularly the long wavelength light (red and near-infrared), to extend the effective path length within the active silicon layer and subsequent light trapping inside the absorber material of the solar cell [9, 10], wet chemical etching of the AZO thin films has been adopted to develop the textured surface for enhancing the efficiency of solar cells [11]. In this study, diluted hydrochloric acid (HCl) etching of the GZO thin films has been carried out at room temperature to develop the textured surface, and we will prove that this structure can enhance the efficiency of the n-i-p α -Si:H solar cells.

In this work, the properties of the GZO thin films grown on glass substrates by RF sputtering process under different substrate temperatures (room temperature (RT), 100°C, 200°C, and 300°C, resp.) were first studied. X-ray diffraction (XRD) pattern, surface morphology observation, hall measurement, and optical transmittance ratio were used to monitor the changes in the structural, optical, and electrical properties. Thin film Si solar cells using hydrogenated amorphous Si (α -Si:H) and nanocrystalline Si (nc-Si:H) are among the most well-developed thin film photovoltaic materials. After the optimal substrate temperature was found, the GZO thin films with thickness of 1000 nm were deposited at that parameter. Finally, the GZO thin films were etched by HCl solution with different concentrations, and then they were used as the electrodes to fabricate the α -Si:H thin-film solar cells. The current-voltage properties of the fabricated thin-film solar cells were also investigated to prove that the textured structure formed by etching process could improve the efficiency of the fabricated thin-film solar cells.

2. Experimental Details

In this work, RF (13.56 MHz) magnetron sputtering process was used, and ZnO (97 wt%, 5 N) doped with Ga₂O₃ (3 wt%, 5 N) was mixed, ground, calcined at 1000°C for 5 h, and sintered at 1400°C to form the ceramic targets with 2 inch in diameter. The used substrates were 33 mm × 33 mm × 2 mm glass. Before the deposition process was started, the base chamber pressure of sputtering system was pumped to less than 1×10^{-6} Torr, and then the deposition parameters were controlled at different pressures and powers. The optimal deposition parameters were RF power of 50 W and working pressure of 5×10^{-3} Torr because the deposited GZO thin films had the most flat surface and acceptable deposition rate. The GZO thin films were also deposited at different substrate temperatures, where room temperatures (RT); 100°C, 200°C, and 300°C were used.

Thickness of the GZO thin films was one of the most important parameters to influence the characteristics of the superstrate p-i-n α -Si:H thin film solar cells. For that, thickness of the GZO thin films was measured using a Nano-View SEMF-10 ellipsometer and confirmed by field emission scanning electron microscopy (FESEM), and deposition rates and film thickness of the GZO thin films were determined by averaging five data obtained by FESEM. For comparing the electrical and optical properties, the thicknesses of the GZO thin films were controlled at about 300 nm by controlling the deposition time. Calculating the observed results, the deposition rate of the GZO thin films first increased from 5.71 nm/min to 5.89 nm/min as the substrate temperature raised from RT to 100°C, reached the maximum of 6.66 nm/min at 200°C, and then decreased to 6.44 nm/min as the substrate temperature was further increased to 300°C. As the substrate temperature increased from RT to 200°C, the GZO molecules have higher active energy for deposition and the deposition rate increases. As substrate temperature is 300°C, the GZO molecules will have too much active energy and hit with each other; for that the deposition rate decreases.

Optical transmittances of the GZO thin films were measured by using a UV-VIS spectrophotometer. The electrical properties of the GZO thin films were determined by a Hall effect measurement. After the physical, optical, and electrical properties of the GZO thin films were measured, the thicknesses of the GZO thin films under the optimal deposition temperature (200°C) were extended to 1000 nm. The surfaces of the GZO thin films were etched by wet etching performed in diluted HCl solution with concentrations of 0.0% (as deposited), 0.1%, 0.2%, and 0.5% in H₂O to acquire the textured GZO thin films. The thickness of the etched GZO thin films was around 660 nm, which was obtained by controlling the etched time of the GZO thin films. The total, normal, diffusion, and haze transmittance ratios of the GZO thin films were measured by using Nippon Denshoku NDH-2000.

Superstrate p-i-n α -Si:H thin film solar cells were fabricated using a single-chamber PECVD unit at 200°C on the etched GZO/glass substrates, as Figure 1 shows. The working pressure was 700×10^{-3} Torr and the deposition power was 20 W. The p-type α -Si (thickness was about 20 nm) was deposited by controlling the gas flowing rates of H₂ = 100 sccm, SiH₄ = 20 sccm, CH₄ = 10 sccm, and B₂H₆ = 40 sccm; the i-type α -Si (about 400 nm) was deposited by controlling the gas flowing rates of H₂ = 100 sccm and SiH₄ = 10 sccm; the p-type α -Si (about 50 nm) was deposited by the gas flowing rates of H₂ = 100 sccm, SiH₄ = 20 sccm, and PH₃ = 20 sccm, respectively. The thicknesses of the all thin films were controlled by the deposition time. The current-voltage characteristic of the fabricated solar cells was measured under an illumination intensity of 300 mW/cm² and an AM 1.5 G spectrum, and all measurements were performed at room temperature.

3. Results and Discussion

Because the GZO thin films deposited at different substrate temperatures had the different crystalline results, the XRD

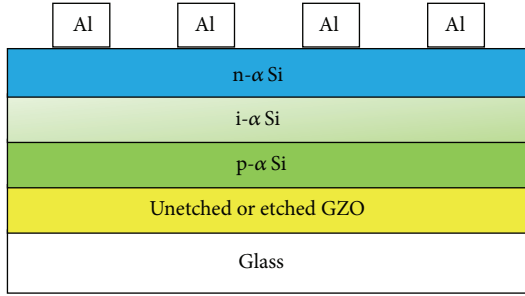


FIGURE 1: Structure configurations of the hydrogenated amorphous silicon thin film solar cells.

patterns of the GZO thin films were investigated at substrate temperatures of RT, 100°C, 200°C, and 300°C. XRD patterns of the GZO thin films are compared in Figure 2, and all the GZO thin films exhibited the (002) peak. The diffraction intensity of (002) peak critically increased as the deposition temperature increased from RT to 200°C and had a maximum at 200°C, and the (004) peak was only observed in 200°C-deposited GZO thin films. The (002) peaks of the GZO thin films deposited at RT, 100°C, 200°C, and 300°C were situated at $2\theta = 33.98^\circ$, 34.04° , 34.11° , and 34.18° , respectively. The lattice constant c was calculated by using the 2θ value, and the calculated lattice constants (c) were 0.5273, 0.5264, 0.5254, and 0.5245 for substrate temperatures that were RT, 100°C, 200°C, and 300°C, respectively. All the calculated lattice constant c of the GZO thin films being smaller than those of the ZnO thin films is considerable, because the radius of Ga^{3+} ions (62 pm) is smaller than that of Zn^{2+} ions (72 pm).

The transmission ratios of the GZO thin films under substrate temperatures of RT~300°C plotted against wavelengths in the region of 300–800 nm were measured with different substrate temperatures as the parameters (not shown here), and the optical transmission at visible region of 400–700 nm was more than 83.5% and had a maximum of 86.2%. Those results prove that the substrate temperature has no apparent influence on the transmission ratio of the GZO thin films on glass substrates. In the transmission spectra of the GZO thin films, as the substrate temperature increased from RT to 200°C, the optical band edge was shifted to lower wavelength.

Figure 3 shows the variations of the carrier concentration, carrier mobility, and resistivity of the GZO thin films deposited by rf magnetron sputtering under different substrate temperatures. The carrier mobility and carrier concentration of the GZO thin films also first increased with raising substrate temperature, achieved the maximum at 200°C, and then decreased for further raising the substrate temperature. The 200°C-deposited GZO thin films had the maximum carrier mobility ($17.08 \text{ cm}^2/\text{V}\cdot\text{s}$) and carrier concentration ($6.97 \times 10^{20} \text{ cm}^{-3}$), respectively. When the GZO thin films are deposited on the glass substrates by using RF sputtering process, many defects result and inhibit electron movement. As the different substrate temperatures are used during the deposition process, the higher substrate temperature enhances the densification and crystallization, which will decrease the numbers of defects and pores in the GZO thin films that will cause the increase in the inhibiting of

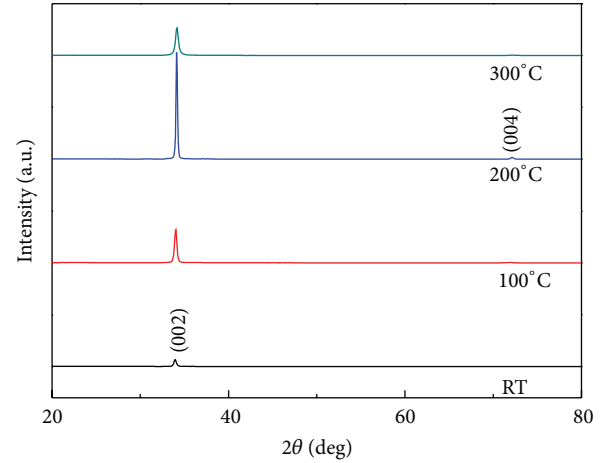


FIGURE 2: XRD diffraction patterns of the GZO thin films deposited on different substrates as a function of deposition temperature.

the barriers electron transportation [12]. The results in Figure 3 prove that as the substrate temperature increases from RT to 200°C, the increases of both the carrier concentration and carrier mobility with raising substrate temperature are attributed to the enhancement in the crystallinity of the GZO thin films.

Figure 3 also shows the dependence of resistivity of the GZO thin films on substrate temperatures. In this study, the carrier mobility and carrier concentration increased with raising substrate temperature and reached a maximum at 200°C. The resistivity of the GZO thin films is proportional to the reciprocal of the product of carrier concentration N and mobility μ :

$$\rho = \frac{1}{Ne\mu}. \quad (1)$$

As (1) shows, both the carrier concentration and the carrier mobility contribute to the conductivity. The minimum resistivity of the GZO thin films at a substrate temperature of 200°C ($5.25 \times 10^{-4} \Omega\cdot\text{cm}$) is mainly caused by the carrier concentration being at its maximum.

The 200°C-deposited GZO thin films have the optimal crystallinity and the smallest FWHM value (Figure 2), the largest carrier concentration and carrier mobility and the smallest resistivity (Figure 3), and acceptable transmittance ratio. For that, the thickness of the 200°C-deposited GZO thin films is extended to around 1000 nm by controlling the deposition time for further HCl-etched process and the fabrication of the p-i-n α -Si:H thin-film solar cells. Figure 4 shows the surface morphologies of the etched GZO thin films as a function of HCl solution concentration, and the etched time was about 30 s. The surface of the as-deposited GZO thin film exhibited a relatively smooth granular structure, as Figure 4(a) shows. Comparing the results shown in Figures 4(a), 4(b), 4(c), and 4(d), the surface roughness increased significantly after HCl etching, and the etching process caused the thin films' surface to develop a crater-like surface structure.

Lo et al. investigated monolayer structure that 500 nm-diameter ZnO spheres were grown on ZnO thin-films' surface

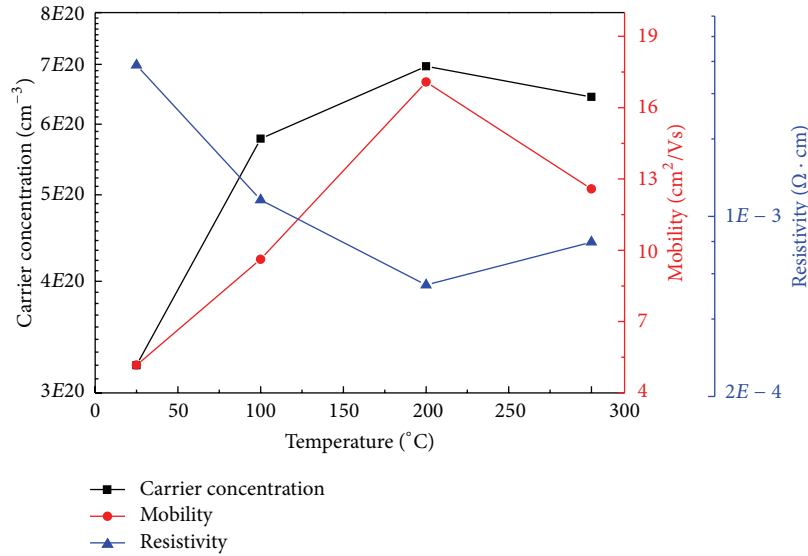


FIGURE 3: Variations of the Hall mobility, carrier concentration, and resistivity as a function of the GZO thin films deposited under different substrate temperatures.

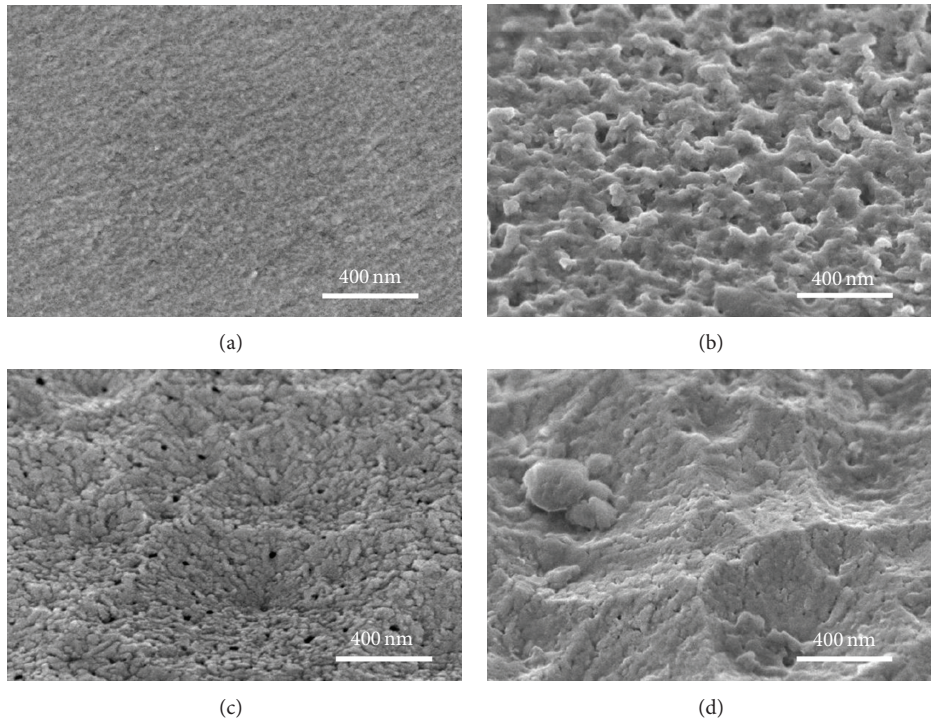


FIGURE 4: Surface morphologies of the etched GZO thin films; (a) as deposited, (b) 0.1%, (c) 0.2%, and (d) 0.5%, respectively.

using sol-gel method. The monolayer-structure thin films exhibit broad-band transparency and a high haze ratio, and they can be used as a light-trapping structure in an ultrathin solar cell [13]. In this study, the etched process is used to increase the haze ratio. As the etched results of the GZO thin films are compared, size surface crater-like caves increased importantly with increasing HCl concentration. The haze ratio of the films before and after HCl etching was measured

as a function of HCl concentration using a haze meter (Nippon Denshoku, NDH 2000). However, the total, normal, diffusion, and haze transmittance ratios of the GZO thin films are measured from the results shown in Figure 5, and the results are shown collected in Table 1. As Table 1 shows, the total transmittance ratio had no apparent change; thus, the normal transmittance ratio decreased, and the diffusion and haze transmittance ratios increased with increasing HCl

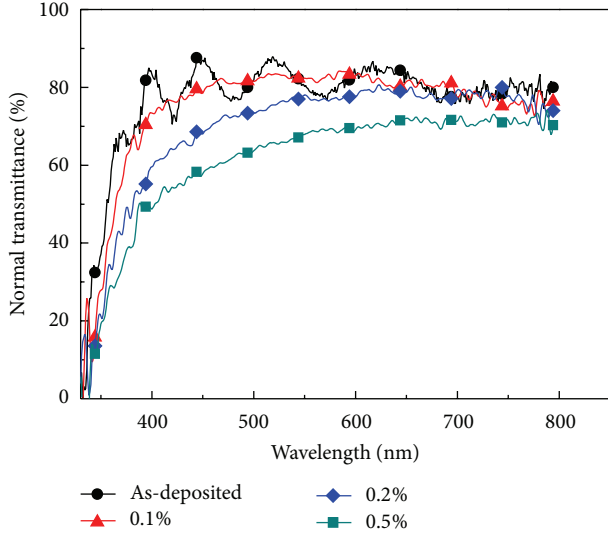


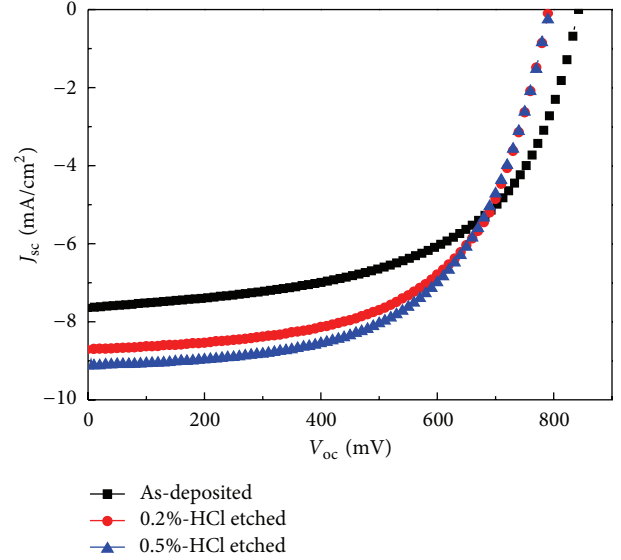
FIGURE 5: Haze transmittance of the HCl-etched GZO thin films.

TABLE 1: Total, normal, diffusion, and Haze transmittance ratios as a function of etched HCl concentration.

Parameter	As deposited	0.1% HCl	0.2% HCl	0.5% HCl
Total (%)	82.39	83.55	81.51	81.37
Normal (%)	81.24	80.88	74.36	65.40
Diffusion (%)	1.15	2.68	7.15	15.97
Haze (%)	1.44	3.21	8.87	19.60

concentration. Haze ratios of the as-deposited, 0.1% HCl-etched, 0.2% HCl-etched, and 0.5% HCl-etched GZO thin films, were 1.44%, 3.21%, 8.87%, and 19.6%, respectively, revealing that the etched GZO thin films would effectively scatter an incident light and enhance light trapping inside the absorber material of thin film solar cells. From the HCl-etched surfaces shown in Figure 4, the increases of roughness and the sizes of caves will cause the increase of light scattering. That is believed to be the reason to cause the decrease of the total transmittance ratio and the increase of haze transmittance ratio.

Superstrate p-i-n hydrogenated amorphous silicon thin film solar cells were fabricated using a single-chamber PECVD unit at 200°C, and the structures of the designed solar cells are shown in Figure 1; no antireflective coatings were deposited on the cells. Figure 6 shows the measured current-voltage characteristics of the fabricated solar cells (substrate size $3.3 \times 3.3 \text{ cm}^2$) under illumination. The values of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and efficiency (η) are measured for the devices using the deposited and with 0.2% HCl-etched and 0.5% HCl-etched GZO thin films as the front transparent conductive thin films. For substrates of as deposited, 0.2% HCl-etched and 0.5% HCl-etched GZO thin films were used, and the V_{oc} values of the solar cells were 0.837 V, 0.790 V, and 0.791 V; the J_{sc} values were 7.66 mA/cm², 8.71 mA/cm², and 9.13 mA/cm²; the FF values were 0.502, 0.525, and 0.545; the efficiency values were 3.22 ± 0.12 , 3.66 ± 0.09 , and $4.02 \pm$

FIGURE 6: Current-voltage characteristics of the p-i-n α -Si:H thin-film solar cells under illumination.

0.13, respectively. As we know, the fill factor and efficiency of the solar cells are listed below:

$$FF = \frac{I_{mp} V_{mp}}{I_{sc} V_{oc}}, \quad (2)$$

$$\eta = \frac{P_{max}}{P_{in}} \times 100\% = \left[\frac{(FF)(I_L)(V_{oc})}{P_{in}} \right] \times 100\%.$$

As (2) shows, I_{sc} , (J_{sc}), and V_{oc} are the important factors to influence the efficiency of the fabricated solar cells. The greater efficiency in using the 0.5% HCl-etched GZO thin films is mainly ascribable to that the Haze ratio of the GZO thin films increased with increasing HCl concentration, and that would effectively enhance light trapping inside the absorber material of solar cells and then increase short-circuit current density and improve the efficiency of the fabricated thin-film solar cells.

4. Conclusions

In this study, the 200°C-deposited GZO thin films had the maximum carrier mobility and carrier concentration of $17.08 \text{ cm}^2/\text{V}\cdot\text{s}$ and $6.97 \times 10^{20} \text{ cm}^{-3}$ and minimum resistivity of $5.25 \times 10^{-4} \Omega\cdot\text{cm}$, respectively. The haze ratios of the etched 200°C-deposited GZO thin films increased from 1.44% to 19.6% as the concentration of HCl solution increased from 0.0% (nonetched) to 0.5%. As the concentration of the etched HCl solution increased from 0% to 0.5%, even the V_{oc} value of the solar cells decreased from 0.837 V to 0.791 V, thus the J_{sc} value increased from 7.66 mA/cm² to 9.13 mA/cm², the FF values increased from 0.502 to 0.545, and the efficiency increased from 3.22 ± 0.12 to 4.02 ± 0.13 , respectively. This study proves that the etching process on the transparent electrodes (GZO thin films) is good choice to improve the efficiency of the fabricated amorphous silicon thin film solar cells.

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