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Short Communication

Ag/Cu plating to improve Ag grid electrodes of the recycled c-Si solar cells

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More and more crystalline silicon (c-Si) solar cells, which are dominating the photovoltaic (PV) application, will be decommissioned after the service term due to the performance degradation. It will be valuable if the degraded c-Si solar cells can be recycled for reuse. For this, to restore the performance of the recycled c-Si solar cell becomes important. Here, we developed a two-step Ag/Cu electroplating method to repair Ag grid electrodes of the degraded c-Si solar cell. Such repair improved aspect ratio and excellent conductivity of the repaired Ag/Cu finger electrodes were obtained. Meanwhile, the absolute efficiency value of the repaired c-Si solar cell had 118% improvement after the Ag/Cu plating repairing process. In addition, the two-step plating Ag/Cu process is easy to operate, economic and friendly to the environment. These results demonstrated that the two-step electroplating Ag/Cu could be a promising method to repair and reuse the degraded c-Si solar cells.

Keywords: electroplating, electrode repair, recycled c-Si solar cell

1. INTRODUCTION

As an attractive renewable energy, photovoltaic (PV) energy has been paid much attention for several decades. Till now, plenty of PV modules have been installed all over the world. Most of the installed modules are crystalline silicon (c-Si) modules [1]. However, with the increase of service time, the performance of c-Si PV modules will gradually degrade. More and more c-Si PV modules will be decommissioned after the service term due to the performance degradation. Till 2050, the estimated amount of the decommissioned PV modules can be up to about 9.57 million tons [2]. The c-Si PV modules are composed of abundant Si, Al, Cu, Ag, glass, etc. It is necessary to recycle the decommissioned c-Si PV modules to avoid environmental pollution and at the same time to save the limited material resources. The material recycling is usually realized by destruction or chemical etching [3-5]. If some valuable components, such as c-Si solar cell, can be reused, a lot of energy and material resources can be saved. However, as a prerequisite, the degraded performance of the solar cell must be restored. Usually, the separation or peeling of the Ag grid electrodes is one of the main reasons for the performance degradation of the c-Si solar cell [6]. Therefore, it will be valuable if an effective way can be found to repair the Ag electrodes for the recycled c-Si solar cells.

The Ag grid electrodes of the c-Si solar cell are normally prepared by screen-printing of Ag paste, followed by a high-temperature sintering [7-9]. The Ag paste is mainly composed of three components: Ag particles, glass frit and organic solvent [10]. During the sintering process, the organic solvent in the paste is evaporated and the antireflective layer on the surface of the c-Si solar cell (mainly silicon nitride) is etched through by the glass frit [11]. At the same time, the Ag grid electrode is developed via interaction and fusion of Ag particles and finally attached to the c-Si solar cell by glass etching and penetrating into the antireflective layer [12]. Such formed Ag electrode is not dense and has a lot of holes inside [13]. It might be detached during its use to make the solar cell performance degrade.

It is impossible to repair the degraded Ag grid electrodes by screen-printing and sintering again. On one hand, it is difficult to print accurately on top of the old electrodes. On the other hand, the c-Si solar cell cannot afford the high-temperature sintering for the second time, which will result in a severe destruction of the solar cell structure inside.

Another way to make electrodes is electroplating [14,15], during which the plating layer can be deposited onto the certain conductive regions by applying an appropriate voltage in the electroplating bath. However, the Ag grid electrodes of the recycled c-Si solar cells are usually greatly damaged. A simple Ag electroplating to repair the electrodes of the recycled c-Si solar cells will consume too much amount of Ag.

Here, we proposed a two-step Ag/Cu plating process based on the use of Cu capping layer on top of Ag seed layer. Firstly, the Ag seed layer was deposited by light induced plating (LIP) [16] onto the old Ag grid electrodes. The formed Ag crystallites could be filled into the grid voids to make the grid electrodes much denser. The Ag seed layer also behave as a diffusion barrier which prevents copper from diffusing into the bulk silicon. Final step, so-called step-growth, in this process the seed layer is thickened by electroplating deposition of Cu layer [17]. Due to this, we can achieve high aspect ratio and excellent conductivity performance of the recycled c-Si solar cell greatly.

2. EXPERIMENTAL

2.1. Pretreatment of the recycled c-Si solar cell

The recycled c-Si solar cell was obtained by thermal decomposition of the c-Si PV module. Al frame and cable box of the module were removed mechanically first. Then, the plastic back sheet was also peeled off mechanically with an assistant of hot wind heating. The obtained glass panel with c-Si solar cells attached on the surface by the encapsulate was put into a Muffle furnace for thermal decomposition treatment at about 500 °C. The pyrolysis of the organic encapsulate would result in the c-Si solar cell detachment from the glass panel. At last, the recycled c-Si solar cell was cleaned in deionized water and dried.

2.2. Electroplating baths

Ag Electroplating bath was composed of silver nitrite (0.25 M $AgNO_3$) and ammonium sulfate (1M $NH_4)_2SO_4$). Sodium hydroxide (1 M NaOH) was used to balance the pH value to 7.

Cu electroplating bath was composed of anhydrous cupric sulfate (0.25 M $CuSO_4$) and sodium hydroxide (1 M NaOH) to regulate the pH value to 7.

2.3. Two-step plating of Ag and Cu layers

Light-induced plating of Ag seed layer: The recycled c-Si solar cell was attached firmly onto a Ag plate so that the back electrode of the solar cell could be completely separated from the Ag plating solution. Then the LIP process was carried out in the Ag plating bath at 30 ºC with a 1000 W/m^2 light irradiation to stimulate photo-generated current for 1 minute. During the plating process, the bath was stirred constantly.

Electroplating of Cu layer: The c-Si solar cell after Ag light-induced plating was put into Cu electroplating bath at room temperature and the bath was also kept stirring. A DC (direct current) voltage was loaded onto the electrodes to keep the plating current density as 0.5 A/dm2 for 2 minutes.

2.4. Measurements

The current–voltage (*I*–*V*) characteristics of the c-Si solar cells before and after the Ag/Cu plating reparation were measured by the *I*–*V* tester (GSOLA®, Solar Cell Tester) with AM1.5 sun simulator. The line resistance of the grid electrode was measured by the four-probe method. The morphology of the surface and cross-sectional microstructure of the Ag grid electrodes were observed by using scanning electron microscopy (SEM, CARL ZEISS, SIGMA), and the element distribution at the cross-sections were analyzed by using the Energy Dispersive Spectrometer (EDS, Apollo X, EDAX).

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of the degraded Ag grid electrodes without repair. The width of the Ag grids is about 30 μm and the height is 10 μm, as shown in Fig. 1a. Figure 1b shows that the Ag particles are hexagonal at the surface of Ag grids. There are many holes inside the Ag grids, as shown in Fig. 1c. The holes are in the size of several micrometers.

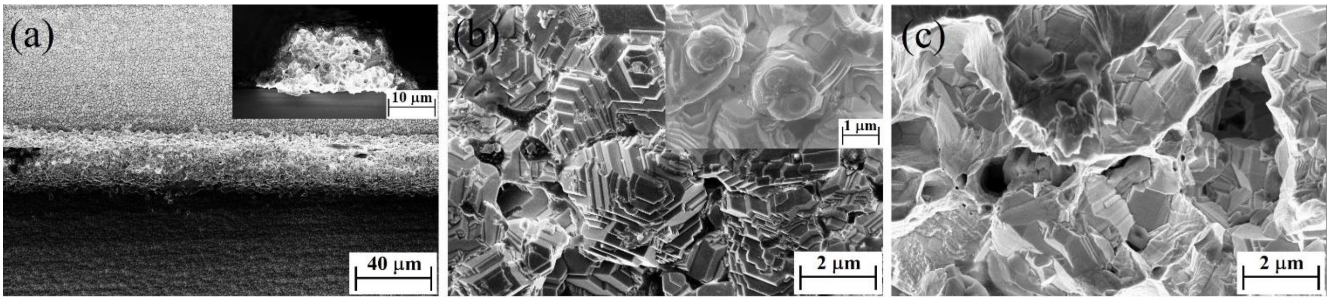

Figure 1. SEM images of Ag electrodes before repair, (a) the surface of the Ag grid and the inset is the cross-section of the Ag grid; (b) the magnified surface of the Ag grid and the inset is the surface of the sintered Ag particles; (c) the magnified cross-sectional image of the Ag grid.

Figure 2 shows the SEM graphs of the Ag grids after Ag light-induced plating. The width of Ag grids increases to 35 µm and the height increases to 15 µm as shown in Fig. 2a. And Fig. 2b shows the grid surface after Ag light-induced plating is covered by spherical grains, which are about 1 µm in grain-size. Meanwhile, there is no gap between the light-induced plated Ag and the original Ag grids as shown in Fig. 2c. Due to the size of new plated Ag grains is less than 500 nm as shown in Fig. 2d, the holes inside the original Ag grids are fulfilled with the new Ag grains, which makes the Ag grids much denser.

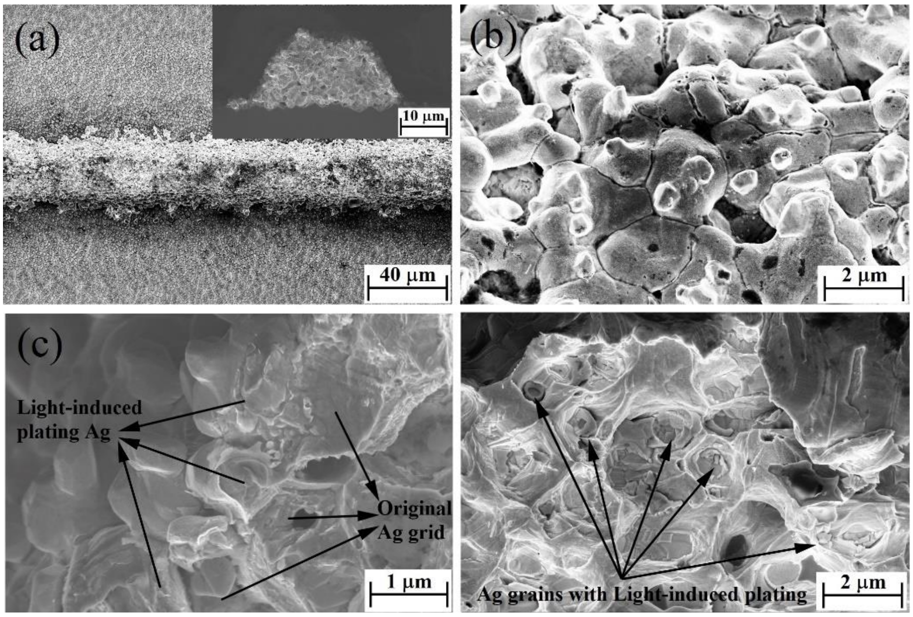

Figure 2. SEM images of Ag electrodes after Ag light-induced plating, (a) the surface of the Ag grid and the inset is the cross-section of the Ag grid; (b) magnified surface of the Ag grid; (c) and (d) magnified cross-section of the Ag grid.

Figure 3 shows the SEM micrographs of the Ag grids after Cu electroplating further. Fig. 3a is the morphology of the grid surface, which shows the grid width has increased to 150 µm, and the inset is its corresponding cross-sectional morphology, showing that the height of Ag grids has increased to

60 μm after Cu electroplating. The large increase of the grid size indicates that the growth rate of the Cu film by electroplating is faster than that of Ag by the light-induced plating. So, Cu electroplating can rapidly increase the cross-sectional area and reduce the resistance of the grid electrodes. As shown in Fig. 3b, the Cu film is formed by the compact growth of cubic Cu grains in the size of about 1 μm. There does not exist any hole in the Cu film. Figure 3c shows that the interior of the grid electrode is thus very dense. Meanwhile, the connection between the Cu film and the Ag film is also tight without gap.

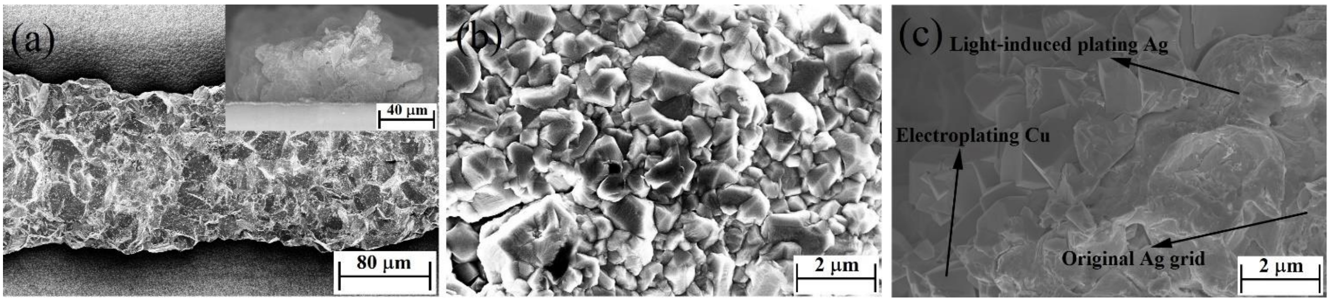

Figure 3. SEM images of Ag electrodes after Cu electroplating, (a) the surface of the Ag grids and the inset is the cross-section of the Ag grids; (b) magnified surface of the Ag grids; (c) magnified cross-section of the Ag grids.

Figure 4 is the EDS analysis result of the grid electrode after the two-step Ag/Cu plating. Location ① is in the Cu film and the measured result shows that the Cu film is highly pure. Location ② is in the Ag seed layer formed by the light-induced plating and the result shows that the Ag element is the dominating component.

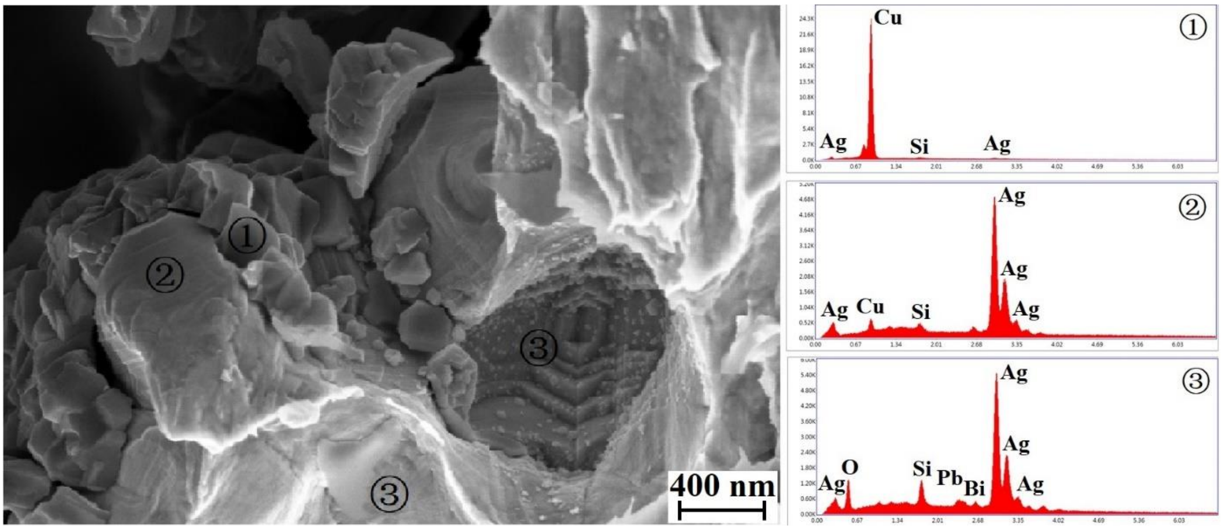

Figure 4. EDS of the grid electrode on the recycled c-Si solar cell after Ag/Cu plating repair.

But trace amounts of Cu and Si element are also detected in the Ag seed layer. This indicates that some Cu atoms have diffused into the Ag film. Location ③ is inside the original Ag grid. Besides Ag, Pb, Bi and O elements from the glass frit are also presented. Importantly, no Cu element has been found. This indicates that Cu atoms do not enter the interior of the old Ag grids due to the obstruction of the Ag seed layer. So the possibility of Cu diffusion risk into the c-Si solar cell can be avoided effectively.

Table 1 and Figure 5 show the electrical performance of the recycled c-Si solar cell before and after the Ag/Cu grid electrode repair. As can be seen from Table 1, the series resistance of the solar cell is very large without repair, indicating that the Ag gird electrodes are damaged seriously, so that the short-circuit current, fill factor and conversion efficiency of the recycled c-Si solar cell are all low. After repair by the light-induced plating of Ag, the series resistance of the solar cell is reduced significantly. Meanwhile, the open-circuit voltage, short-circuit current, fill factor and conversion efficiency are all improved. After the following electroplating of Cu, the electrical performance of the solar cell is further improved. In addition, the line resistivity of the Ag/Cu plating repaired electrodes is just a little higher than the Ag plating repaired electrodes (as shown in Fig. 6). Both resistivities are very close to the resistivity of the original Ag paste sintered electrodes [18], so that adopting Cu instead of Ag to repair the Ag grid electrodes of the recycled c-Si solar cells has little effect on its conductivity. However, the increase in the cross-sectional area of the Ag grids significantly reduces the series resistance of the c-Si solar cells and thus improves the conversion efficiency of the solar cells. As a demonstration in Table 1, the conversion efficiency of the recycled c-Si solar cell has been improved from 8.23% to 18%. a 118% improvement after the Ag/Cu plating repair process is achieved. Although the efficiency is a little less than that of today's cells, it has achieved 90% of what it was four years ago [19, 20]. Therefore, using the two-step Ag/Cu plating to repair the Ag grid electrodes can effectively improve the performance of the recycled c-Si solar cells, and make them reusable.

Table 1. Electrical performance of the recycled c-Si solar cell before and after electroplating repair treatment.

No.	V_{oc}/V	I_{sc}/A	R_s/Ω	R_{sh}/kΩ	FF/%	E_{ff}/%
before repair	0.575	7.820	0.0351	0.130	44.57	8.23
After Ag plating	0.627	8.541	0.0165	0.471	62.56	13.78
After Cu plating	0.649	9.356	0.0074	0.667	72.09	18.00

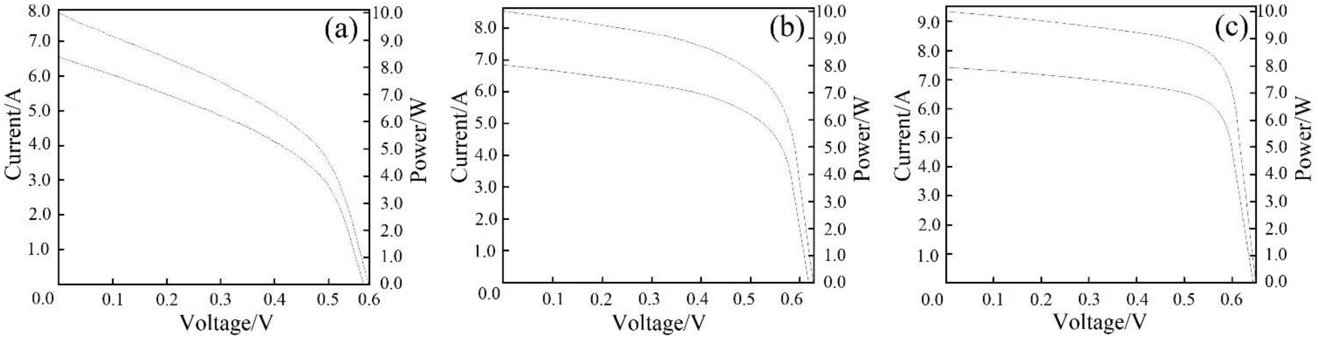

Figure 5. *I-V* curves of the recycled c-Si solar cells; (a) before repair; (b) after Ag light-induced plating; (c) after Cu plating.

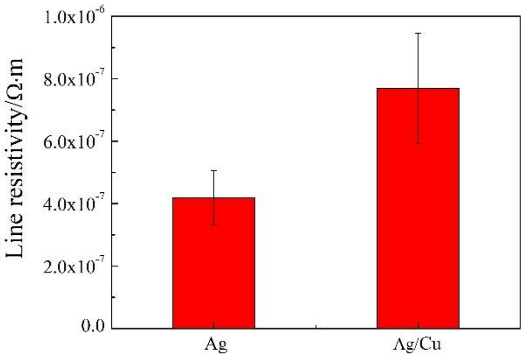

Figure 6. The line resistivity of the repaired electrodes with Ag plating and Ag/Cu plating.

Figure 7 shows the pictures of the Ag grid electrodes for the recycled c-Si solar cell before and after Ag/Cu plating repair. Fig. 7a is a picture of the c-Si solar cell without repair, and it can be seen that the c-Si solar cell has many seriously broken and peeled Ag grids, especially the busbar of the c-Si solar. Therefore, the fill factor and conversion efficiency of the solar cell are very low, and the series resistance is very large as shown in Table 1. Meanwhile, these destructions of Ag grids also induce great difficulty for electroplating process. The electroplating current cannot be uniformly distributed to make the plated layer continuous. The formation of the Ag seed layer by light-induced plating can preliminary repair these broken and peeled sites. Fig. 7b shows the repaired grid electrodes after the two-step Ag/Cu plating, which indicates the effectiveness of the two-step Ag/Cu plating.

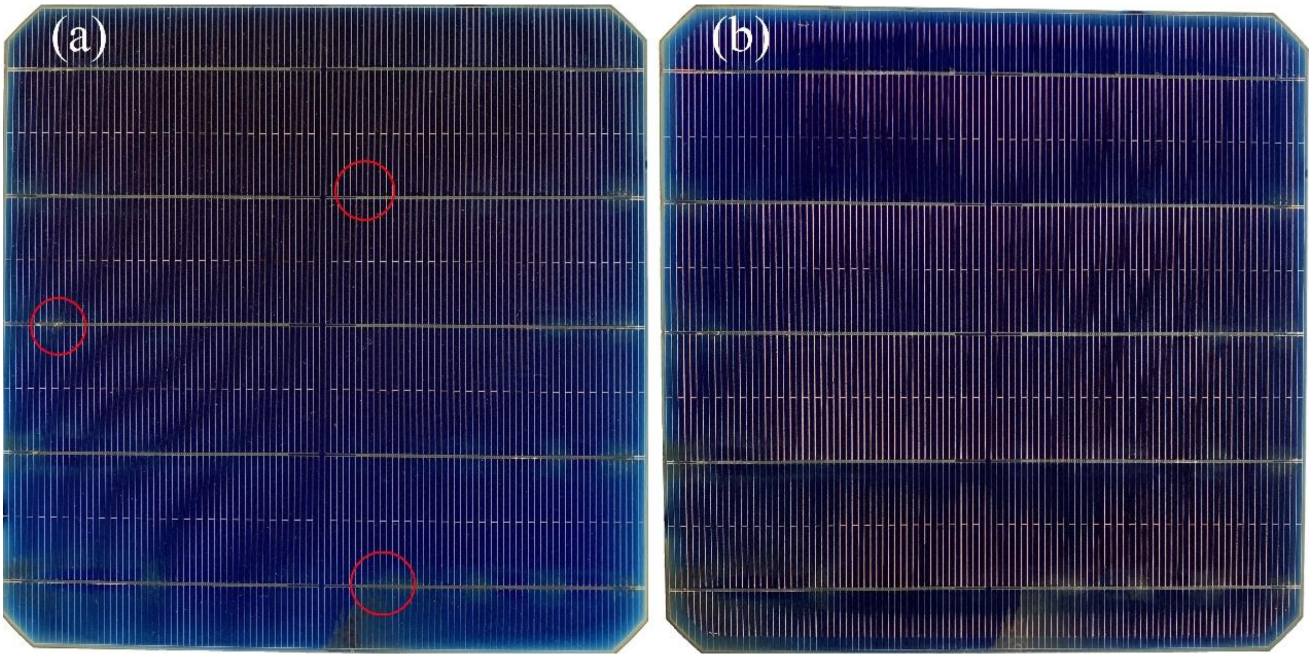

Figure 7. The pictures of c-Si solar cells. (a) Before Ag/Cu plating repair; (b) After Ag/Cu plating repair**.**

4. CONCLUSION

A two-step Ag/Cu plating method was proposed to repair the degraded Ag grid electrodes of the recycled c-Si solar cells. Firstly, the Ag seed layer was deposited by light induced plating (LIP) onto the old degraded Ag grid electrodes, including the grid-broken and peeled sites. The formed Ag crystallites could fill into the grid voids to make the grid electrodes much denser. The Ag seed layer also behaved as a diffusion barrier to prevent the subsequent copper from diffusing into the bulk silicon. Secondly, the Cu capping layer was electroplated onto the Ag seed layer to make the grid electrodes wider and higher. By the two-step Ag/Cu plating, high aspect ratio and excellent conductivity could be achieved for the grid electrodes, which would improve the performance of the recycled c-Si solar cell greatly. As a demonstration, a 118% enhancement of the absolute solar cell efficiency was obtained after the Ag/Cu plating. The results show that the proposed two-step Ag/Cu plating could be an effective way to restore the performance of the recycled degraded c-Si solar cells and make them valuable for reuse.

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