

# Elimination of small-sized Ag nanoparticles via rapid thermal annealing for high efficiency light trapping structure



Yiming Bai<sup>a,b,\*</sup>, Zheng Gao<sup>b</sup>, Nuofu Chen<sup>a,b</sup>, Hai Liu<sup>b</sup>, Jianxi Yao<sup>a,b</sup>,  
Shuang Ma<sup>b</sup>, Xiaoqiang Shi<sup>b</sup>

<sup>a</sup> State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, 102206 Beijing, China

<sup>b</sup> Renewable Energy School, North China Electric Power University, 102206 Beijing, China

## ARTICLE INFO

### Article history:

Received 8 April 2014

Received in revised form 8 June 2014

Accepted 7 July 2014

Available online 12 July 2014

### Keywords:

Ag nanoparticles

Rapid thermal annealing

Film rupture mechanism

Light trapping structure

## ABSTRACT

Since the small-sized metallic nanoparticles (NPs) show high absorption ratio, eliminating small-sized NPs to obtain high efficiency light trapping structure in photovoltaic devices is particularly necessary. In the present work, we successfully restrained the formation of small-sized Ag NPs via magnetron sputtering followed by rapid thermal annealing, which is driven by the film fluctuation and rupture mechanism of dewetting theory. Relatively, a 10.73% increase of short-circuit current density was achieved when Ag NPs fabricated by rapid thermal annealing were used as light trapping structure of solar cells. This study validates the necessity of eliminating small-sized NPs experimentally and theoretically, which is helpful for obtaining high efficiency light trapping structure and understanding the metallic film annealing mechanism.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

In the recent 10 years, noble metallic nanoparticles (NPs) have been attracting growing interest and studied extensively in the photovoltaic communities due to their light trapping property [1–3]. As a new kind of light trapping structure, NPs can help solar cell capture more photons of incident light and therefore inadequate absorption in thin film solar cells can be overcome effectively [4]. The effectiveness of light trapping greatly depends on the polarizability of metallic NPs, which relies on the shape, size, refractive index, surface coverage rate and environmental medium [5]. Generally, the extinction is dominated by the absorption of metallic NPs when their sizes are much smaller than the wavelength of light. Therefore, high ratio of small-sized NPs will weaken the light trapping effect [6]. However, although large-sized NPs are very helpful for light trapping in photovoltaics owing to their enhanced light scattering property [7], the over high order modes, such as quadrupole, may suppress the light scattering in the visible light, if

the size exceeds a threshold [8]. Therefore, optimizing the size of NPs to increase light scattering and suppress absorption makes a great difference for achieving high efficiency light trapping structure of solar cells.

Physical and chemical methods have been adopted to prepare the NPs with various sizes to improve the efficiency of solar cells [9–11]. Compared with the chemical methods, physical methods with post annealing have attracted much more attention due to their unique advantages, such as compatible process with solar cells, good repeatability, simple and non-toxic. However, physical methods, such as magnetron sputtering and thermal evaporation with conventional in situ (IS) annealing, may induce the extremely wide range of particle size distributions [12–14], especially a large number of small-sized NPs appeared, which is unfavorable for the light trapping. Therefore, two aspects of this problem need to be addressed. The first question involves how to suppress the formation of small-sized particles to obtain high efficiency light trapping structure. Although NPs with uniform size can be acquired through the template method, an increase in cost is accompanied. The second problem relates to the demonstration of the mechanism for eliminating small-sized NPs. However, most studies pay attention to the effectiveness of plasmonic NPs [15], few works are available on suppressing the formation of small-sized NPs by physical methods with post annealing, much less of the demonstrations of

\* Corresponding author at: State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, 102206 Beijing, China. Tel.: +86 10 61772455.

E-mail addresses: [yimbai@ncepu.edu.cn](mailto:yimbai@ncepu.edu.cn), [yimbai@semi.ac.cn](mailto:yimbai@semi.ac.cn) (Y. Bai).

its mechanism. It is expected that the question will be resolved and the mechanisms will be illuminated effectively with the approach proposed in this work.

To clearly understand the negative effects of small-sized NPs, the absorption ratio (AR) and extinction spectra for Ag NPs with different sizes were calculated according to the Mie theory in this paper. Our results confirm that the AR decreases with the increase of the NPs' diameter, and Ag NPs with diameter of 100 nm show high light trapping efficiency. Furthermore, a careful experiment study has been performed for suppressing the formation of small-sized NPs. The Ag films with different thicknesses were deposited on poly-crystalline silicon (PC-Si) thin film solar cells by magnetron sputtering, and then rapid thermal annealing (RTA) or conventional IS annealing were carried out. We found that RTA can restrain the formation of small-sized NPs compared with that of conventional IS annealing, and the mechanism is demonstrated in this work based on the film rupture mechanism of dewetting theory [16,17]. As expected, the optical test results of NPs are in consistent with the theoretical simulation. The performance measurement of PC-Si thin film solar cells with Ag NPs fabricated by different annealing modes is in accordance with the optical test results and strongly supports the mechanism proposed above.

## 2. Experiment

The Ag films were deposited on plain glasses and PC-Si thin film solar cells by MS-JB550A magnetron sputtering equipment, respectively. Prior to the deposition, the substrates were cleaned by ultrasonication sequentially in acetone, ethanol and deionized water for 5 min, and then dried with nitrogen. The sputtering chamber was evacuated to a base pressure of  $1.0 \times 10^{-5}$  Pa, and then filled with the high purity Ar (99.999%) sputtering gas with a constant flow rate and the working pressure maintained at 0.5 Pa. After pre-sputtering for 10 min, the Ag films were deposited at room temperature for 80, 100 and 120 s with the direct-current power of 20 W, and the resulting thickness of Ag films are 6, 7.5 and 9 nm, respectively. A series of samples were annealed in situ at 500 °C under vacuum condition for 1 h with a temperature rising rate of 0.33 °C/s, and then they were brought to room temperature for natural cooling. The corresponding samples were labeled as Ag-IS-1, Ag-IS-2 and Ag-IS-3 for the initial Ag film thickness of 6, 7.5 and 9 nm, respectively. Another series of films deposited under the same conditions were annealed at 500 °C for 1 h under a nitrogen atmosphere by RTA with the heating rate of 100 °C/s. The corresponding samples were labeled as Ag-RTA-1, Ag-RTA-2 and Ag-RTA-3.

In this work, high quality PC-Si thin film were fabricated on graphite substrates by the so-called "seed layers approach". This method relates to a two-step process in which a very thin PC-Si seed layer with (004) preferential orientation is first deposited, and then thick film is grown on this layer by chemical vapor deposition. The same technique can refer to the investigation of Auer et al. [18]. Before deposition the seed layer, a p-ZnO blocking layer deposited by JB-650 radio-frequency magnetron sputtering equipment was inserted between the substrate and seed layer to reduce the influence of graphite pore on silicon. Lastly, the PC-Si thin film solar cells were obtained by forming p-n hetero-junction. Fig. 1 illustrates the schematic diagram of PC-Si thin film solar cell structure with Ag NPs, and the area of solar cells is  $1 \text{ cm} \times 1 \text{ cm}$ .

The surface morphologies were analyzed by scanning electron microscopy (SEM, Quanta 200F). The optical properties were measured by an ultraviolet-visible spectrophotometer (UV spectrophotometer, Cary 5000). For the X-ray Diffraction (XRD) measurements in a  $\theta$ - $2\theta$  scan mode, a Panalytical X'Pert-MPD Pro diffractometer with a Cu  $K\alpha$  X-ray source was used. The current

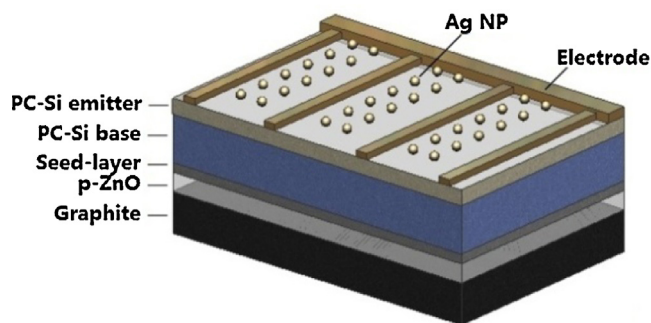


Fig. 1. Schematic diagram of PC-Si thin film solar cell structure with Ag NPs.

density versus voltage ( $J$ - $V$ ) characteristic was measured by Newport 92250A Solar Simulator.

## 3. Results and discussion

In thin film hydrodynamics, when Ag film is annealed, atoms diffuse on the surface and the flat film surface is perturbed into a wavy shape [19]. Namely, the film thickness fluctuation occurs. At this moment, the elastic energy decreases but surface energy increases, and the surface disturbances of all wavelengths tend to enlarge derived from the stress. On the contrary, the increased surface energy is inclined to stabilize disturbances of short wavelengths, but the long wavelengths are excluded [20]. Therefore, the fluctuation of thickness continually enlarges and ruptures, given enough thermal energy supplied. Then, the dewetting starts from holes formed randomly in the film, and a polygon network of connected strings generates. Lastly, the strings break up, shrink and coalesce into NPs [21]. Fig. 2 shows a typical cross-sectional view SEM image of Ag NPs by RTA annealing. As shown in Fig. 2, the NPs demonstrate near-spherical geometrical features. Hence, the spherical model was adopted within the theoretical simulation in this work.

Fig. 3a-c presents the plane-view SEM images of Ag-IS-1-3 respectively. As can be seen, Ag NPs are round in shape, and the mean particle diameter of Ag-IS-3 is the largest while it is the smallest for Ag-IS-1. This can be explained by the relationship between the diameter  $D$  and film thickness  $h$ , which can be described by the equation [22]:

$$D = Ch^{5/3} \quad (1)$$

where  $C$  is a constant related to the geometric factor of NPs. The corresponding surface coverage is 26.7%, 19.1% and 17.4% for Ag-IS-1, Ag-IS-2 and Ag-IS-3, respectively, deriving from an increase of average particle height. Moreover, as shown in Fig. 3, a large number of small-sized NPs were generated during IS annealing process. Fig. 4 shows the statistical diameter distribution histograms of Ag NPs analyzed by Image J software. The numbers of NPs with  $D \leq 50 \text{ nm}$  are 344, 368 and 385 for Ag-IS-1, Ag-IS-2 and Ag-IS-3, respectively.

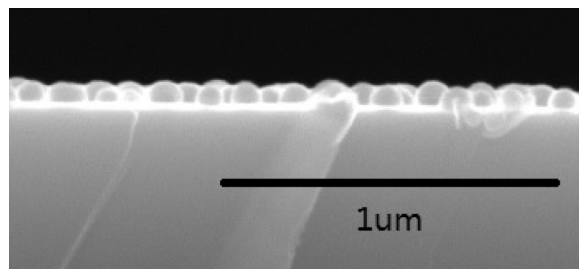


Fig. 2. Typical cross-sectional view SEM images of Ag nanoparticles.

Download English Version:

<https://daneshyari.com/en/article/5351118>

Download Persian Version:

<https://daneshyari.com/article/5351118>

[Daneshyari.com](https://daneshyari.com)