

Improved Photovoltaic Characteristics of Amorphous Si Thin-Film Solar Cells Containing Nanostructure Silver Conductors Fabricated Using a Nonvacuum Process

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This paper proposes a low-cost highly reflective liquid organic nanostructure silver conductor with superior conductivity, using back contact reflectors in amorphous silicon (a-Si) single-junction superstrate configuration thin-film solar cells produced using a nonvacuum screen printing process. The conductive paste is composed of Ag nanowires (Ag NW) mixed with an Ag nanostructure sheet (Ag NS). The paste is referred to as “Ag NWS.” A comparison of silver conductor samples with vacuum-system-sputtered silver samples indicated that the short-circuit current density (J_{sc}) and the open-circuit voltage (V_{oc}) of Ag NWS conductor cells exceeded 0.22 mA/cm² and 66 mV, respectively. The Ag NWS conductor with back contact reflectors in solar cells was analyzed using external quantum efficiency measurements to effectively enhance light-trapping ability in a long wavelength region (580–700 nm). The cells constructed using the optimized Ag NWS demonstrated an increase of approximately 6.1% in power conversion efficiency under AM 1.5 illumination. These results indicated that the Ag NWS conductor back contact reflector layer is a suitable candidate for high-performance a-Si thin-film solar cells

1. Introduction: Hydrogenated amorphous silicon (a-Si:H) thin-film solar cells have received considerable attention in photovoltaic research because of the potential to produce electricity from solar energy on a large scale by using low-cost mass production. Amorphous silicon is a direct-bandgap material, which means that less silicon is necessary for a-Si cells. Furthermore, it can be deposited at temperatures below 300 °C, which allows for deposition on not only glass, but also lightweight flexible substrates such as stainless steel [1, 2]. When employed on large glass surfaces, a-Si module solar panels are highly suited for building-integrated photovoltaic (BIPV) applications and provide excellent protection against the damaging influence of weather (i.e., humidity, rain, dust, snow, hailstones, and particularly the high-energy photons of UV light) [3, 4]. As the volume of photovoltaic manufacturing increases to meet growing market demands, producing environmentally friendly products becomes increasingly difficult. a-Si does not contain heavy metals (e.g., Cd) or rare elements (e.g., In and Te), thus reducing the environmental repercussions of fabrication processes and producing abundant material supplies. These advantages have caused a-Si to become the most reliable and most readily available of all thin-film solar cells; however, several researchers are still attempting to improve the development of high-efficiency a-Si:H photovoltaic technologies to increase the competitiveness of thin-film solar cells on the market and provide a profitable performance-to-price ratio. Recently, several studies have presented novel approaches to improve the short-circuit current (J_{sc}) and conversion efficiency of a-Si thin-film solar cells. In particular, creating an optimal light-trapping scheme is critical. Theuring et al. demonstrated that AZO-Ag-AZO front contact electrodes can be combined with light-trapping mechanisms such as a textured substrate to improve the photocurrent J_{sc} [5]. Islam et al. indicated that both J_{sc} and efficiency tended to improve as Au nanoparticles size increased, because of the increase in light scattered by large Au nanoparticles, creating a plasmonic effect [6]. Lee et al. presented textured GZO films with distinct surface roughnesses prepared using acetic acid-diluted nitric acid solution. Based on the increases of J_{sc} in samples, it was concluded that efficiency was enhanced by surface roughness because of the ability to capture light effectively [7]. de Jong et al. presented a hot-

embossing technique for testing the light-trapping ability of periodically micro-V angle pyramidal-structured polycarbonate substrates, which demonstrated a significant increase in J_{sc} over reference a-Si cells deposited on flat glass substrates [8]. Kim et al. demonstrated a CF4-based plasma texturing treatment process for borosilicate glass in superstrate silicon thin-film solar cells, and observed that the largest reduction in surface light reflectance occurred at low RF power and at optimal processing time, which indicated that the advantage of this treatment method is the increased possibility of light entering the a-Si absorption layer, thus improving cell performance [9]. Cho et al. reported that nanotextured Ag back reflectors (BRs) enhanced the absorption of incoming light and J_{sc} in a-Si solar cells. The optimal-textured Ag BRs film, called “hot silver,” was obtained by depositing the film at a temperature of 500 °C and preparing it in a sputtering system [10, 11]. Based on these findings, these light trapping techniques require careful manufacturing processes of great complexity, as well as use of high temperatures to fabricate optimal-performance cells. Fundamentally, conventional Si thin-film solar cell technology depends on textured metal-based back reflectors, which typically consist of a silver layer deposited on a thin TCO layer, such as ZnO [12]. Although silver reflectors exhibit excellent electrical and optical reflectivity properties, they incur a high manufacturing cost when the sputtering vacuum system is used. From an industrial viewpoint, the silver reflector layer should be manufactured as inexpensively as possible without compromising adequate light trapping. A recent study proposed an alternative approach: a low-cost and highly reflective liquid organic nanostructure-sheet silver conductor, developed as a back-metal reflector layer by using a nonvacuum screen printing process for a-Si single junction p-i-n solar cells [13]. In the current study a paste referred to as “Ag NWS” with a conductor BRs layer composed of Ag nanowires (Ag NW) mixed with Ag nanostructure sheet (Ag NS) was proposed and constructed using the same nonvacuum process as previous cells, and this paste was implemented in the construction of a-Si cells. In contrast to sputtered silver cells, the Ag NWS cells not only retain superior light trapping capability but also achieve more favorable photovoltaic performance.

2. Experimental details:

2.1 Preparation of Nonvacuum Screen Printing Ag NWS Films

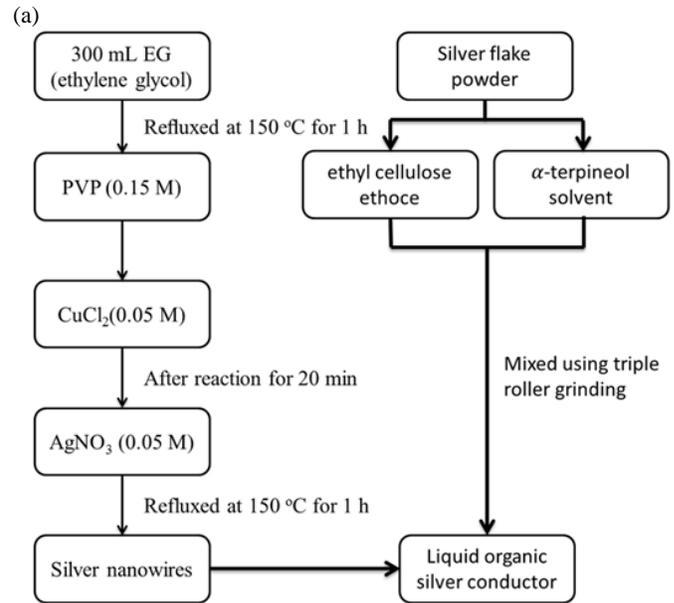
Ag NW was synthesized using an air-assisted polyol method as follows. In a typical synthetic procedure, 300 mL of EG (ethylene glycol) was heated and refluxed in a three-necked flask at 150 °C for approximately 1 h. 50 mL of an EG solution PVP (0.15 M) and 1 mL of CuCl_2 (0.05 M) was added to the solution. After reacting for 20 min, AgNO_3 (0.05 M) in 50 mL of EG was added slowly. The mixture was heated to 150 °C for 1 h, and the color of the solution turned from clear to gray. The cooled solution was then centrifuged several times at 2000 rpm for 15 min to remove excess PVP and other impurities in the supernatant. After centrifugation, the Ag NW precipitate was redispersed in ethanol.

A liquid organic silver conductor containing commercially available silver flake powder, ethyl cellulose ethoce, and α -terpineol solvent was used in this study. The grains of the silver powder varied in particle size, with a particle size distribution of 2 to 25 μm . The mixtures were mixed in a high-speed mixer for 3 min. Subsequently, uniform pastes were formed through triple roller grinding. Finally, the liquid organic silver conductor and Ag NW suspensions were mixed to form the hybrid silver conductor, Ag NWS. The Ag NWS consisted of 70% silver powder and 5% Ag NW. Fig. 1(a) displays a flow diagram of the Ag NWS fabrication process. Fig. 1(b) illustrates the Ag NWS dispersion liquid paste product. The liquid organic Ag NWS conductor, which serves as a BR layer in a-Si devices, was baked on a hot plate at 80 °C. The thickness of Ag NWS was approximately 2 μm and sheet resistivity was 4.9 $\text{m}\Omega/\text{square}$. The sputtered-silver BR layer was constructed using an RF magnetron sputtering vacuum system. Deposition was performed at 300 W at a sputter gas pressure of 5 mTorr in an Argon gas atmosphere. The thickness of the BR layer was approximately 200 nm and sheet resistivity was 3.2 $\text{m}\Omega/\text{square}$. Typical a-Si:H module cells in superstrate configurations were constructed using an interconnected scheme. The interconnection of cells in the module was achieved using the following three steps of laser scribing: TCO cutting, a-Si layer ablation, and back-contact removal, named P1, P2, and P3, respectively. In this study, a nonvacuum screen printing process was used to print a BR layer of liquid organic silver conductor film on a-Si:H module solar cells. Step P3 of the laser scribe process was omitted, consequently shortening the back-contact manufacturing process [13].

2.2. Fabrication of a-Si p-i-n Thin-Film Solar Cells

Amorphous Si (a-Si) single-junction p-i-n solar cells were deposited using a 40 MHz very-high-frequency plasma-enhanced chemical vapor deposition (VHF-PECVD) cluster system. Intrinsic a-Si:H thin films were grown using SiH_4/H_2 gas mixtures that were approximately 350 nm thick at 200 °C. The optical band gap of the intrinsic a-Si:H thin films was 1.75 eV, determined using the conventional Tauc plot method. The photosensitivity characteristics of the a-Si:H thin films were approximately five orders of magnitude [14]. Boron-doped amorphous silicon oxide (p-a-SiO:H) layers were deposited using $\text{B}_2\text{H}_6/\text{SiH}_4/\text{N}_2\text{O}/\text{H}_2$ gas mixtures. The p-layer thickness was approximately 10 nm. Phosphorus-doped microcrystalline silicon n-layers (n- μc -Si:H) approximately 9 nm thick were then deposited in a mixed atmosphere of $\text{PH}_3/\text{SiH}_4/\text{H}_2$ gases. In the p-i-n superstrate configuration, the TCO front contacts layer introduced rough interfaces into the a-Si solar cells. Zinc oxide (ZnO) has received considerable attention because it can withstand deposition at low temperatures and is stable against hydrogen plasma and high temperature processes. Moreover, it possesses a large exaction binding energy of 60 meV and a wide bandgap energy of 3.37 eV [15]. Boron-doped ZnO (ZnO:B) exhibits high transmittance, low sheet resistance, and efficient light scattering, indicating that ZnO:B is an ideal candidate for use as a contact layer in thin-film solar cells [16]. Thus, the front contact material of the devices in this study was

ZnO:B, and deposition was performed using a low-pressure chemical vapor deposition system. One previous study provided detailed parameters and optoelectronic properties of the deposition process [17]. The final device structure was composed of glass/ZnO:B/p-a-SiO:H/i-a-Si:H/n- μc -Si:H/ZnO/Ag. In this study, vacuum-sputtered silver and a nonvacuum liquid organic Ag NWS conductor, using a screen printing process, were used to investigate the light-trapping properties of the cells in various silver BRs. The density-voltage (J-V) test cells possessed an active area of 4.0 cm^2 . The performance of the solar cells was characterized using J-V measurements under standard AM1.5 (100 mW/cm^2) illumination at 25 °C. The external quantum efficiency (EQE) of the solar cells was measured at zero bias voltage to determine the spectral responses at various wavelengths. The optical properties of the BRs were characterized using a PerkinElmer LAMBDA™ 750S UV/Vis/NIR spectrophotometer to measure the total reflection spectra.



(b)



Fig. 1 (a) displays a flow diagram of the Ag NWS fabrication process. (b) illustrates the Ag NWS dispersion liquid paste product.

3. Results and discussion:

Fig. 2 displays the scanning electron microscope photographs of the liquid organic Ag NWS conductor film that was successfully deposited onto a glass substrate surface. The conductive paste was composed of Ag NW mixed with Ag NS. The diameters of the sheet silvers ranged from 2 to 10 μm . The sheet silver conductor film was satisfactorily interconnected during the nonvacuum screen printing

process. The Ag NW were randomly dispersed within the sheet silver, with diameters and lengths of approximately 100 nm and 20 μm , respectively. Such a dense interconnected sheet structure can increase light trapping efficiency by increasing light reflectance. Compared with previous sheet silver experimental results [13], the new Ag NWS electrodes developed in this study possess lower sheet resistivity, from 5.4 to 4.9 $\text{m}\Omega/\text{square}$, indicating that the mixed Ag NW contributed to enhanced contact conductivity. Compared with the sputtering silver process, the nonvacuum screen printing process can more easily achieve large-scale fabrication and low fabrication costs, which can result in rapid commercial adoption.

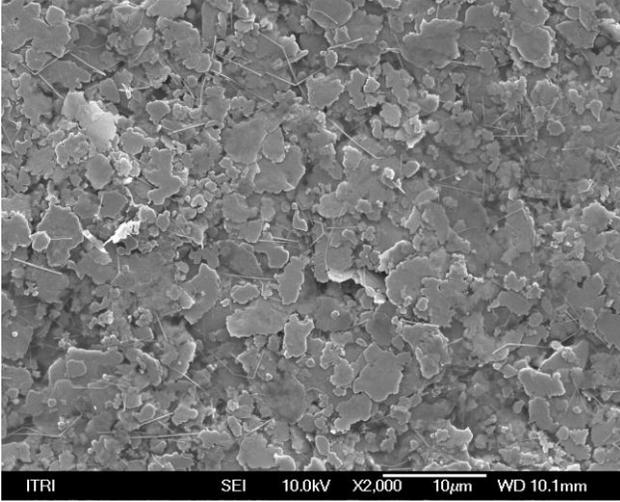


Fig.2 The SEM photographs of non-vacuum liquid organic Ag NWS conductor film deposited on glass substrate surface by screen printing process.

Fig. 3 displays the light reflectance measurements of sputtered silver, liquid organic Ag NS, and Ag NWS conductor films, produced using a nonvacuum screen printing process and deposited on a textured TCO glass substrate. The average total reflectance of the Ag NWS samples obtained from the screen printing process (approximately 49%) was higher than that of the samples obtained from the sputtering process (approximately 38%). The average total reflectance of the Ag NWS conductor film samples was higher than that of the sputtered samples by nearly 27% in the visible light region, indicating that the Ag NWS BR films exhibited superior scattering properties, compared with the high absorption loss and low reflectivity of the sputtered silver BR samples [18]. The reflectance of the Ag NWS samples was slightly lower than that of the Ag NS samples, which might be attributable to a surface plasmon absorption effect caused by Ag NW mixed with Ag NS [19]. Additionally, when the incident light passed through the glass and TCO of a-Si cells and arrived at the textured interface containing silicon, the majority of the light was absorbed; however, the light in the near-infrared (NIR) region was not completely absorbed into the silicon layer, and reached the back contact reflector layer. Therefore, excellent reflectivity in the NIR region is crucial. Rough metal interfaces generally exhibit a lower total reflectance than do smooth metal surfaces [20]. Fig. 3 illustrates that the Ag NWS BR sample exhibited noticeably higher IR reflectivity than the sputtered-silver BR sample did, suggesting that the proposed silver conductor was smooth. This high reflectivity is advantageous and serves to back-reflect the long wavelength light, increase the optical path of absorbed light in the a-Si layer, and improve device performance.

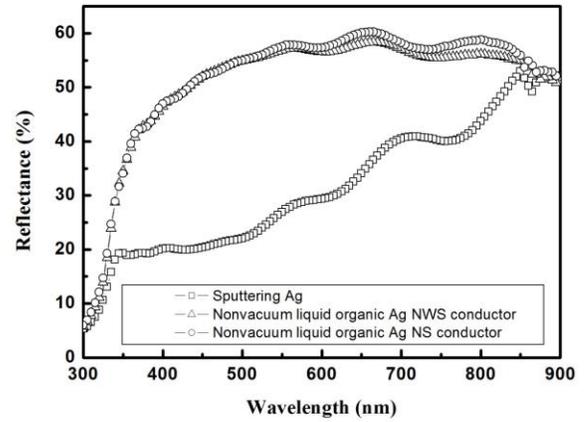


Fig. 3 Light reflectance spectra of sputtering Ag, non-vacuum liquid organic Ag NS and Ag NWS conductor film by screen printing process deposited on textured TCO glass substrate, respectively.

Fig. 4 displays the J-V characteristics of a-Si:H p-i-n solar cells under illumination and subjected to various BR processes. Ag NWS conductor BR films prepared using a nonvacuum screen printing process yielded superior cell performance. Table 1 lists the photovoltaic parameters of the performance of a-Si solar cells with sputtered Ag and nonvacuum liquid organic Ag NWS conductors. An initial active-area efficiency of 5.68% was achieved. Compared with the sputtered silver BR sample, a notable increase in J_{sc} of 0.22 mA/cm^2 was observed when the Ag NWS was introduced as a BR sample, which indicated that the extent of light reflectance, which depends on the Ag NWS conductor, considerably influenced the optical properties of the a-Si solar cells. The trends of the experimental results were consistent with the measured data in Fig. 3. These results indicated that the V_{oc} increased from 697 mV in the sputtered silver BR samples to 763 mV in the Ag NWS samples. Improvement in the V_{oc} of Ag NWS cells can be justified by approximating the ideal solar cell equation for V_{oc} , as illustrated in [21]:

$$V_{oc} = \frac{kT}{q} \ln \left[\frac{J_{sc}(V_{oc})}{J_0} + 1 \right] \approx \frac{kT}{q} \ln \left[\frac{J_{sc}(V_{oc})}{J_0} \right] \quad (1)$$

where k is the Boltzmann constant, T is ambient temperature, q is electrical charge, and J_0 is reverse saturation current, and the photogenerated voltages ($J_{sc}(V_{oc})$) are calculated at $V=V_{oc}$ from dark J-V responses. By using the logarithm of the ratio of $J_{sc}(V_{oc})/J_0$, an increased V_{oc} value was obtained for the Ag NWS cells. Increased V_{oc} is caused by the increment in photocurrent J_{sc} . The optimal sheet silver conductor BRs in a-Si cells presented in a recent study exhibited similar trends [13]. Ag NWS BRs cells displayed greater V_{oc} variation than did sheet silver conductor BRs. This phenomenon can be attributed to the decreased sheet resistivity of Ag NW mixed with Ag NS.

To confirm the superior cell performance of the Ag NWS conductor BRs, EQE curves were measured under a zero bias condition. Generally, light scattering at the back contact plays a dominant role in enhancing the spectral response at wavelengths longer than 600 nm. Fig. 5 displays the EQE spectral responses for a-Si:H p-i-n solar cells achieved using several BR processes. The spectral responses of the Ag NWS BR cells in the red spectral range increased to a level greater than that of the sputtered silver cells (58%–61% at 650 nm). These observations indicated that the Ag NWS conductor improved light trapping at wavelengths longer than 600 nm. In contrast to the Ag NWS conductor cells, the sputtered silver cells exhibited lower

reflectance, which might be related to the poor optical utilization rates, which caused a decrease in J_{sc} . These results are consistent with the expected results derived from the reflectance and J-V measurements displayed in Figs. 3 and 4.

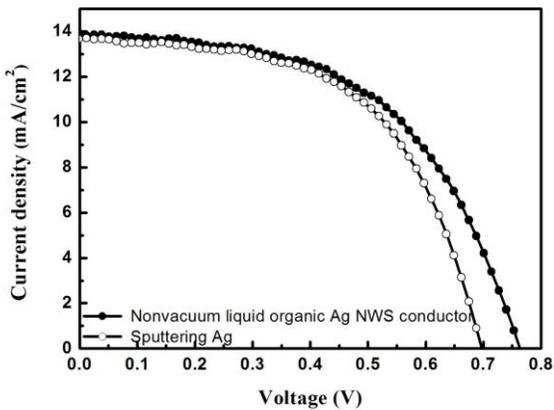


Fig. 4 J-V characteristics for a-Si:H p-i-n solar cells under illumination with different back reflectors process.

Table 1 Performance of a-Si:H p-i-n solar cells with different back reflectors.

Sample	V_{oc} (mV)	J_{sc} (mA/cm ²)	F.F. (%)	η (%)
Sputtering Ag	697	13.67	56.21	5.35
Ag NWS conductor	763	13.89	53.64	5.68

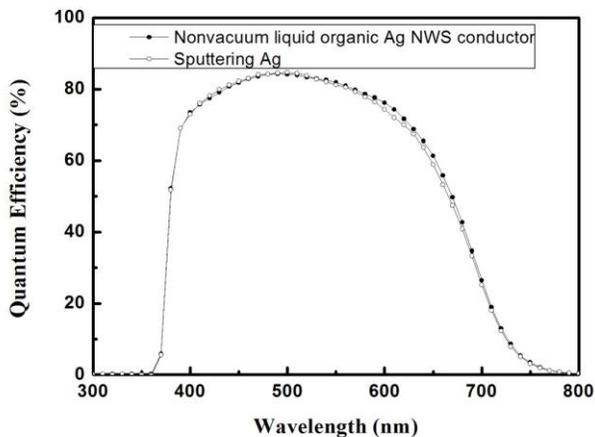


Fig. 5 EQE spectra response for a-Si:H p-i-n solar cells with different back reflectors process

4. Conclusion: This study determined that the proposed highly reflective Ag NWS conductor back contact reflector layer, fabricated using a nonvacuum process, is a suitable candidate for high-performance a-Si thin-film solar cells. The light reflectance, J-V, and EQE measurement results indicated that Ag NWS conductor BR devices yield excellent light-trapping properties. By contrast, sputtered silver BR devices exhibited poor photovoltaic performance because the

rough metal interface exhibited a low total reflectance over the entire wavelength. Using optimal Ag NWS conductor BRs, an optimal initial active area efficiency of 5.68% was achieved. The key reason for this superiority was the improvement of short-circuit current density and the enhancement of BR light-trapping capabilities.

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