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Low-Cost & Low-Temperature Curable Solution-Processed Silica-based Nanostructured Antireflection Coatings on $CuIn_{1-x}Ga_xSe_2$ Thin Film Solar Cells

Seung-Yeol Han[a,b,c], Changqing Pan[a,b], Dae-Hwan Kim [a,b,d], Chih-hung Chang[a,b,c]*

A simple, low-cost & low-temperature curable Silica-based antireflective coatings (ARCs) by a solution-based process has been investigated for Cu(In,Ga)Se_2 (CIGS) solar cells for the first time. Thin layers of nanostructured ARCs that featuring 20~30 nm SiO_2 NPs were fabricated from a simple, low-cost chemical solution. The silica-based nanostructured ARCs were deposited on the glass substrate and on top of the CIGS solar cells. The nanostructured ARCs on glass could increase the transmittance by 3.9%. The nanostructured ARCs could reduce the reflection of CIGS solar cells by 4.96%. The nanostructured ARCs on CIGS solar cells resulted in an enhancement of solar energy conversion efficiency from 16.0% to 17.2%. These enhancements confirm the utility of these simple nanostructured ARCs as a cost-effective solution of photon management in thin film CIGS solar cells.

Introduction

Anti-Reflective Coatings (ARCs) generally consist of one or more layers of dielectric material in the form of a quarter wavelength (QW) thickness film that exhibits a wavelength sensitive reduction in reflection due to optical interference [1]. Kuo *et al.* recently created a seven-layer structure, which includes TiO_2 films and SiO_2 nanorods, using oblique-angle deposition at different angles and achieved an extremely low reflectance for silicon solar cells [2]. The use of more than two layers of ARCs is costly for large area PV applications. Multilayered films require precision and multiple deposition steps can therefore be expensive, thus single layer QW ARC is more commonly used in lower-cost, large area applications. Currently, several lower-cost ARC approaches are being researched for solar cells applications. In 1960, Bernhard discovered a periodic array of sub-wavelength protrusions on the cornea of moths [3]. These so-called "moth-eye" structures work on the principle of a gradient index of refraction [4-6]. These gradient surfaces can be thought to have a low net reflectance based on the destructive interference of an infinite series of reflections at each incremental change in refractive index. More recently, researchers have found that the structures do not need to be periodic, only that the stochastic structure yields features on the whole that are smaller than the wavelength of visible light [7]. Engineers have found a variety of ways to mimick moth-eye nanostructures using ARCs deposited by electron-beam lithography [8], nanoimprint lithography [9], plasma-enhanced chemical vapor deposition (PECVD) and interference lithography [10, 11]. However, these technologies all require high-cost capital equipment which can be difficult to adapt to large area formats required for solar cells and window glass applications. For example, Chen *et al.* reported broadband and quasi-omnidirectional ARCs using an aperiodic array of silicon nanotips by high-density electron cyclotron resonance plasma etching on single crystal silicon [12]. These techniques are too costly for large area solar PV applications. Various antireflective coating studies using MgF_2 have been shown and used for reducing reflectance of the surface of silicon and thin film CIGS solar cells [13-15]. The fabrication of MgF_2 thin films is normally carried out by physical vapor deposition. Physical vapor deposition such as sputtering is well known to be inefficient in terms of energy and material utilization. Recently, a number of research groups have demonstrated the use of nanostructured ZnO as effective ARCs for solar cells [16-19]. Y. Liu *et al.* reports the use of ZnO nanowires as an ARC on micropyramid silicon solar cells with a low reflectance of 3.2% [16]. Han *et al.* reported the growth of ZnO nanorod arrays on a textured silicon substrate using a continuous flow microreactor [17]. Hsieh *et al.* reported an effective approach for enhancing photoelectric conversion of Cu(In,Ga)Se_2 solar cells with three-dimensional ZnO nanotree arrays [18]. Jheng *et al.* reported the use of ZnO nanostructure as effective ARCs for Cu_2ZnSnS_4 (CZTS) thin film solar cells [19]. These nanostructured ZnO ARCs were fabricated using a batch hydrothermal process in the majority of these work. These batch processes require the immersion of the entire solar cells into a bath which is less desirable for manufacturing. Another promising yet lower cost approaches have also been pursued by using silica nanoparticles and dip-coating process to create single layer QW porous silica ARCs on solar cover glasses[20]. This approach was actually developed by Moulton back in 1947 [21]. Most recently DSM developed a single layer inverse porous silica ARC technology, KepriCoat^{TM}. The inverse porous silica layer was created form polymer-silica core-shell particles [22]. The inverse porous structure lowers the surface roughness, increase the scratch resistance, durability, and cleanability. The core-shell particles were synthesized by coating a layer of silica nanoparticles on a spherical cationic polymer template. For example, a cationic polymer particle with a diameter around 80nm is used as template. Tetramethyl orthosilicate was added to the polymer solution to form core-shell particles. The reaction is stopped by dilution with alcohol followed by subsequent acidification with nitric acid. The core-shell particles were then mixed with inorganic silica binders to form a coating dispersion. The coatings were applied on both sides of the substrate by dip coating. The pores were then generated by removing the polymer particles during the tempering step.

In this study, a simple low-cost and low-temperature curable AR coating solution was introduced and the effectiveness of this nanostructured ARC for CIGS solar cells and for bare glass substrate were demonstrated.

Experimental

The deposition of antireflective coating was carried out on the surfaces of bare glass substrates and functional $CuIn_{1-x}Ga_xSe$ thin film solar cells. Functional $CuIn_{1-x}Ga_xSe_2$ (CIGS) solar cells and films were fabricated at the Daegu Gyeongbuk Institute of Science and Technology (DGIST). CIGS thin films were grown on 60 nm thickness of Mo-coated soda-lime glass substrates through a three-stage process involving the co-evaporation of Cu, In, Ga, and Se. The three-stage process in detail has been described [23]. In the first step, an $(In,Ga)_2Se_3$ precursor was deposited on the substrate for 1500 seconds at 420 °C. In the second step, the Cu-rich CIGS films were grown with Cu and Se fluxes at 550 °C. In the third step, small amount of In and Ga was evaporated to convert the Cu-rich CIGS films to Cu-poor CIGS films. The Se beam flux was kept constant throughout the deposition process while the rate of Ga evaporation was varied. The average 2 μm thickness of the CIGS film was obtained. A CdS buffer layer was deposited on the CIGS films by using a chemical bath deposition (CBD) method. CdS thin film was deposited an aqueous solution containing cadmium sulphate ($CdSO_4$), thiourea (CH_4N_2S) and ammonium hydroxide (NH_4OH). 1:50 molar ratio of cadmium sulphate and thiourea was employed. The aqueous solution was maintained at 60 °C and deposited for 20 min. the deposited CdS thin film was annealed at 200 °C for 2 min on hot plate and a 60 nm thickness of CdS thin film was obtained. Subsequently, 50 and 300 nm thicknesses of i-ZnO and Al-doped ZnO (Al:ZnO) window layers were deposited by rf-sputtering, respectively. Finally, an Al electrode as the front contact was deposited by using a thermal evaporator.

MoreSun^{TM}, sol-gel silica-based Antireflective coating (ARC) solution was supplied by the CSD Nano, Inc. The silica nanoparticles (NPs), size of 20 ~ 30 nm are well dispersed in alcoholic based solution. The glass substrates (3.2 mm Pilkington low iron glass) were cleaned with detergent and washed with DI water, acetone and isopropanol alcohol (IPA). The cleaned glass substrates were dried by flowing air and keep in dust-free container until applying AR coating. The AR coating solution was deposited on bare glass substrates and on CIGS solar cells by spin coating. The thickness of AR coating layer was varied and optimized on the glass substrate by changing rotating speed and then the optimized condition of AR coating deposition was transferred to the surface of CIGS solar cells. The AR coated CIGS cell samples were dried at 100 °C for 10 min in a vacuum oven to evaporate solvents and water. The optical properties, transmittance and reflectance of AR coated on glass substrate and CIGS cell were studied using UV-Vis/NIR spectrophotometer (JASCO V-670) equipped with a 60 mm integrating sphere. Quantum efficiency (QE) of the solar cell was measured by using a real time quantum efficiency tester, Flash QE (Tau Science). The morphology and crystal structure of the CIGS films were measured by using the scanning electron microscopy (SEM, Hitachi Co., S-4800), Atomic Force Microscopy (AFM) (Vecco Innova SPM) and transmission electron microscopy (TEM, Hitachi Co., HF-3300). The electrical properties of completed CIGS solar cells were investigated by using photocurrent (PC) spectroscopy and current-voltage (I-V) curves for a solar simulator at AM 1.5G illumination.

Results and discussion

To optimize AR coating effect on the CIGS solar cells, MoreSun^{TM}, sol-gel silica-based Antireflective coating (ARC) was demonstrated on glass substrate prior to apply for the CIGS solar cells. Commercially available sol-gel silica-based AR coating solution (MoreSun^{TM}, CSD Nano, Inc. USA) provides a low-cost alternative to ARCs fabricated by vapor-phase techniques. The chemical solution has good long-term stability with additional benefits of forming durable thin films via a low-temperature curing process. This solution can be applied by various solution coating processes such as spin coating, dip coating, roll-to-roll slot die or gravure coating, and aerosol spray coating. The simple spin coating process was used on single sided glass substrate for this study. The single sided AR coated glass was cured on a hotplate at 100 °C for 10 min in an ambient air condition. The cured nanostructured ARC shows good durability against a paper wipe test.

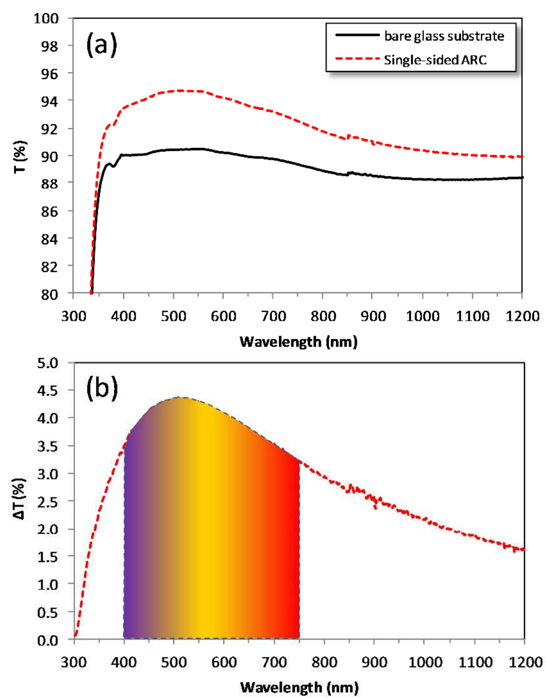

Figure 1. Optical transmittance of (a) single-sided AR coating layer deposited on glass substrate and bare glass substrate, (b) enhancement of transmittance from single-side AR coating, ΔT.

This level of scratch resistance is sufficient because the ARC layer on CIGS cell will be covered underneath the EVA layer and the cover glass in a solar module assembly. More detailed mechanical and stability testing data for MoreSun^{TM} coatings on solar cover glass are available from CSD Nano, Inc. To evaluate the optical performance of single-sided AR coating, transmittance measurement was carried out over the wavelength range of 300 ~ 1200 nm which is the spectral response range of CIGS solar cells as shown in figure 1. The most effective wavelength range of both solar radiation and CIGS spectral response is 400 ~ 750 nm which is the range of visible light spectrum. The sample deposited by spin coating process was optimized to enhance the optical transmittance in this range and it showed an average increase in transmittance of 3.9% over the wavelength range of 400 ~ 750 nm compared to that of bare glass substrate as shown in figure 1b. The thickness of the ARC layer sample for optimized optical transmittance was investigated by SEM. In figure S1, 130 nm thickness of porous and well-packed uniform silica NPs layer was formed. The thickness of 130 nm is well matched for quarter wavelength of peak transmittance at 510 nm as well. The AFM image and roughness profile are shown in figure S2a and b. The silica-based nanostructured ARCs possess a nano-scale roughness, root mean square (RMS) = 2.92 nm as shown by the AFM analysis. The RMS indicates that the uniformity of ARC layer is very smooth but it has nano feature as moth-eye structure. The mimic moth-eye feature could be additional benefit to enhance the reflection reduction as well. In order to investigate the structure on the top surface of the CIGS solar cells and ARC layer, AR coating on the surface of CIGS solar cells could be observed in the SEM image as shown as in Figure 2.

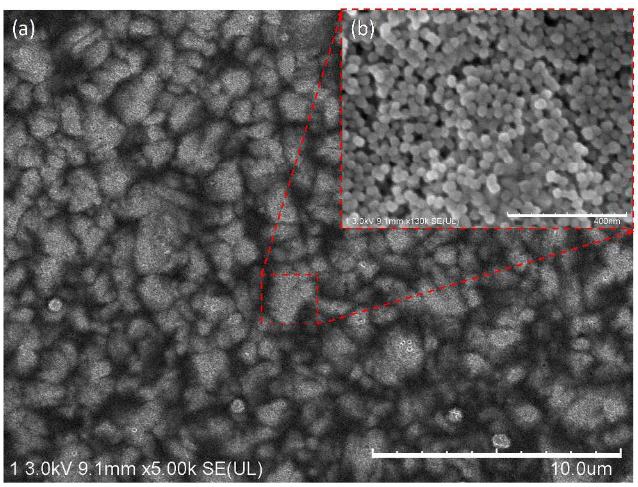

Figure 2. Top-view SEM images of AR coated on the surface of CIGS solar cell: (a) low magnification (10 um scale bar) and (b) high magnification (insert, 400 nm scale bar).

The clear contrast from the image shown in figure 2a could be attributed to the bumpy surface with micro-scale roughness of CIGS layer after a significant grain growth process. More detailed structure characterization of AR coating on the surface of CIGS solar cell was carried out by the cross sectional TEM analysis which are given in the figure 3.
The image shows a textured surface of Al-ZnO/i-ZnO/CdS film stacks on the top of large-grain, highly-crystalline CIGS absorber layer with an average of 2 μm thicknesses.

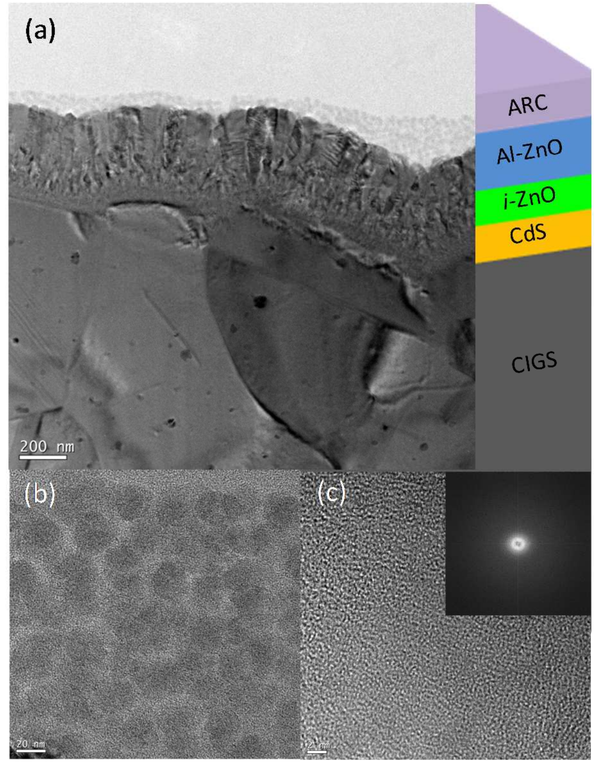

Figure 3. TEM images of (a) Cross sectional CIGS solar cell with ARC layer, high resolution TEM image of (b) silica NPs AR coated layer and (c) silica NP (insert: diffraction pattern of silica NP).

A thin layer of silica NPs was observed on the top of the CIGS solar cells. The thickness of silica-based nanostructured ARC layer on the CIGS solar cells was not uniform due to the limitation of the spin coating process. The use of an optimized spray processes should be able to improve the uniformity. The nanostructured silica layer shows a porous structure which leads to a low index of refraction because of air in the porous layer of silica-based layer as shown in figure 3a & b. However, in micro-scale roughness, the textured surface of the CIGS solar cells was still retained since the thickness of silica layer is less than 200 nm, as shown in figure 2a & 3a. The SEM and TEM images given in figure 2b & 3b show a thin layer with high porosity that is consisted of NPs with a uniform size around 20 ~ 30 nm. The electron diffraction pattern taken from the silica-based nanostructured ARC layer shown in Figure 3c indicates an amorphous structure.

To evaluate the optical performance of the antireflective coating on the CIGS solar cells, the reflectance measurements with an integrating sphere were carried out over the UV-visible to Near-IR spectral range, 300 ~ 1200 nm, as shown in Figure 4. The average reflectance of a bare CIGS film without grid was measured to be 7.70% in the visible wavelength range, 400 ~ 750nm. After applying the silica-based nanostructured ARCs on top of the CIGS solar cell, the average reflectance was significantly reduced to 2.80%, which corresponds to a 4.90% reduction in reflectance. CIGS solar cells (with grid, Al electrode) with/without AR coating show much high reflectance, 8.99% and 13.95%, respectively because of reflection from the Al grids.

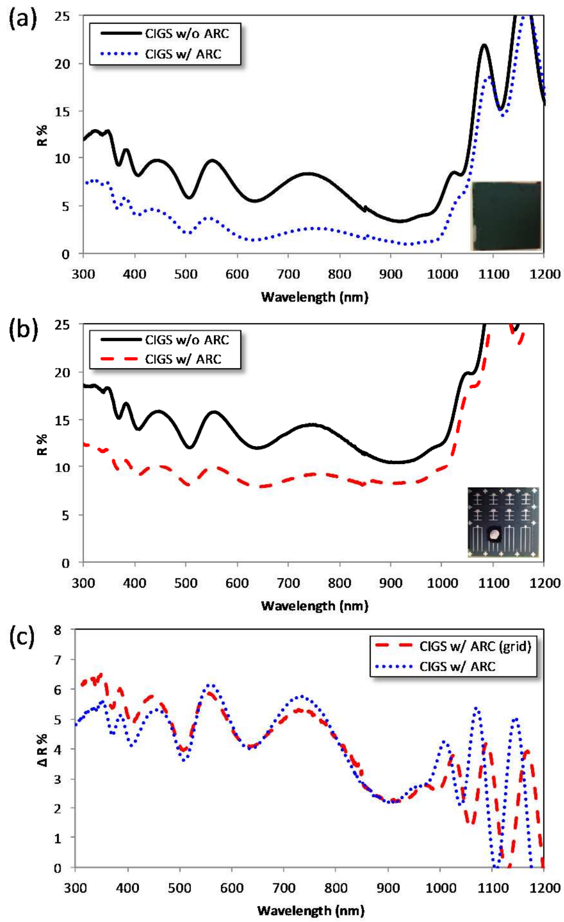

Figure 4. Reflectance of (a) CIGS film with and without AR coating, (b) CIGS solar cell (w/grid) with/without AR coating and (c) enhancement, ΔR% of anti-reflectivity of CIGS thin film and solar cell (w/grid).

The reduction of reflectance is 4.96%, which is similar to the value of reduction from CIGS cell without the Al grids. 4.0% reduction of reflectance was obtained from either sample over the UV-visible to Near-IR wavelength range of 300 ~ 1200nm. The reduction of reflectance, 4.96% over the UV-visible wavelength range, is not the highest value from AR coating on CIGS or other solar cells in view of previously published works [14, 15, 18, 24-26]. For example, MgF_2/SiN_x double layer ARC has been used commercially for reducing reflectance of the surface of silicon solar cells [14, 15]. However, high-cost, low-throughput vacuum-based PVD and CVD are needed for the fabrication of these double layer ARCs. Lower-cost, solution-based techniques have been explored for the fabrication of nanostructured ZnO ARCs for both silicon and thin film solar. Nanostructured ZnO antireflective coatings with a reduction of reflectance from 4.68 ~ 7.5% was demonstrated from these work [18, 24-26]. However, the fabrication of these nanostructured ZnO AR coatings has been mostly performed by the immersion of entire solar cells within a batch hydrothermal reactor, which might pose some limitation for large scale manufacturing. In our previous work, nanostructured ZnO ARC on textured silicon was demonstrated with reduction of reflectance up to 7.2% [17] by using a facile continuous solution process, which could resolve some of the issues of batch hydrothermal reactor. The reduction of reflection from the silica-based nanostructured ARC by spin coating shows a comparable result with the one from the hydrothermal approach. The current approach offers a simpler, cheaper, and more scalable ARC solution than the batch hydrothermal technique. For example, the silica-based solution could be transferred to an aerosol-based spray coating process. The thickness of silica-based AR coating layer on the top of CIGS solar cell as shown in Figure 3a is not uniform because of the nature of spin coating. Spin coating is designed to spread a fluid to the edge of the substrate leaving a thin film of fluid on a flat surface by centripetal acceleration. However, the top surface of CIGS solar cell is not flat. The highly textured surface created valley for tapping more fluids which resulted in a thicker film. It is believed that a more uniform silica-based AR coating on CIGS solar cells can further increase the reduction of reflection towards more than 4.90%.

The CIGS solar cells were measured to evaluate the effect of silica-based nanostructured ARC layer on the performance improvement of external quantum efficiency (EQE) as shown in figure S3. The CIGS solar cells with silica-based nanostructured ARC show an excellent improvement of quantum efficiency, 4.60% as much as the enhancement of the reduction of reflection, 4.90%.

The photovoltaic J-V characteristic was measured to evaluate the effect of silica-based nanostructured ARC on the performance of CIGS solar cells as plotted in figure 5 and the electrical parameters for all CIGS solar cells with/without the nanostructured ARC are summarized in Table 1. The performance of CIGS solar cells with silica-based nanostructured ARC were also measured before and after drying the solar cells at 100 °C for 10 min.

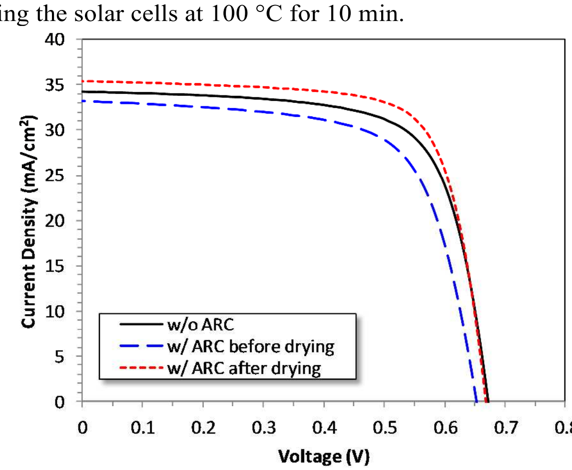

Figure 5. J-V characteristics of CIGS solar cells with and without SiO_2 NPs antireflective coatings

Table 1. Photovoltaic performance of the CIGS solar cells with and without SiO_2 NPs antireflective coatings

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	F.F. (%)	Eff. η (%)	Improvement η (%)
CIGS solar cell w/o ARC	0.67	34.2	69.8	16.0	-
CIGS solar cell w/ ARC before drying	0.65	33.2	67.0	14.5	-1.5
CIGS solar cell w/ ARC after drying	0.67	35.4	72.7	17.2	+1.2

The CIGS solar cell without AR coating achieved a conversion efficiency (η) as high as 16.0% with open-circuit voltage (V_{oc}) = 0.67V, short-circuit current density (J_{sc}) = 34.2mA/cm^2, and fill factor (FF) = 69.8%. The silica-based nanostructured ARC coated CIGS solar cells before and after the drying process show an solar energy conversion efficiency, η of 14.5% and 17.2% with V_{oc} =0.65 and 0.67V, J_{sc} =33.2 and 35.4 mA/cm^2, and FF =67.0 and 72.7%, respectively. After applying the silica-based coating on CIGS solar cell without drying, the performance of the CIGS solar cells decreased significantly because of residue of solvent and moisture from the AR coating solution and atmosphere. Olsen *et al*.[27] indicated that the dominant effect of moisture is a result of increased sheet resistance in the TCO layer. The effect of moisture ingress into the structure of thin film solar cells on J_{sc} and fill factor is significant. Therefore, J_{sc} decreases as a result of increase in sheet resistance and series resistance as well as the fill factor. In table 1, J_{sc} and fill factor of silica-based nanostructured ARC on CIGS solar cell before drying decreased significantly compared to CIGS solar cell without AR coating. As a result of decreased J_{sc} and fill factor, the efficiency decreased from 16.0% to 14.5%. However, the benefits of silica-based nanostructured ARC on CIGS solar cell were demonstrated after removing residual solvent and moisture within the ARC coated CIGS solar cells. The drying condition of 100 °C for 10 min in a vacuum oven does not degrade the performance of the CIGS solar cells which had been proven by several performance tests at the same condition. After drying the short circuit, J_{sc} of nanostructured silica-based ARC coated CIGS solar cells increased significantly from 33.2 mA/cm^2 to 35.4 mA/cm^2. The fill factor also increased from 67% to 72.7%. Simply adding the low-cost, silica-based nanostructured ARCs on top of the CIGS solar cell, J_{sc}, fill factor and the solar energy conversion efficiency increase from 34.2, 69.8 and 16.0 to 35.4 mA/cm^2, 72.7% and 17.2%, respectively. The benefit of adding this simple and low-cost ARC layer on CIGS solar cell is clearly seen from the 1.2% energy conversion efficiency gain. It is believed that further improvement from the nanostructured ARCs could be obtained after optimizing the film thickness and gradient of index of refraction via porosity control. The optimum thickness for maximizing the reduction of reflection would be roughly quarter wavelength thickness, $\lambda/4$ with a single layer coating. Appropriate solution-based deposition technique is currently being explored to optimize the performance of silica-based nanostructured ARCs for CIGS solar cells.

Conclusions

A simple, low-cost & low-temperature curable silica-based nanostructured antireflective coating (ARCs) by a simple solution process was investigated for Cu(In,Ga)Se_2 (CIGS) thin film solar cells for the first time. The SEM and TEM characterizations show a porous silica layer that is consisted of NPs with a uniform size around 20 ~ 30 nm. The electron diffraction pattern taken from the ARC layer indicates an amorphous structure. The obtained silica-based nanostructured ARC shows a significant reduction of the reflection that results in bring in more photons into a solar cell. The silica-based ARCs on bare glass substrate show an increase of 3.9% optical transmittance and the AR coating on CIGS solar cells reduced the reflectance from 13.95% down to 8.99% which corresponding to a 4.96% reduction. This significant reduction of photon reflection within the UV-visible wavelength range resulted in bringing in more photons into the CIGS solar cells. These additional photons increase the solar energy conversion efficiency value by 1.2%. This improvement is very attractive in view of its benefit to the cost ratio and ease of processing. Further studies are needed to transfer this low-cost solution into CIGS module in terms of photon management. First of all, we will need to put our ARCs on the cover glass. Secondly, investigation of adding EVA layer on top of AR coated GIGS layer will also need to be carried out.

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Notes and references

[a]School of Chemical, Biological & Environmental Engineering, Oregon State University, Corvallis, Oregon 97331, United States
[b]Oregon Process Innovation Center, Microproducts Breakthrough Institute, Corvallis, Oregon 97330, United States
[c]CSD Nano, Inc., 720 NE Granger Ave. STE #B2, Corvallis Oregon 97330, United States
[d]Green Energy Research Division, Daegu Gyeongbuk Institute of Science & Technology, Daegu, Korea

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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