The Fabrication of Micro-/Nano-Structural Antirefraction Coatings Based on the PDMS Film for Solar Cells Application

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Abstract. A simple and low-cost methodology to fabricate micro/nanostructure anti-refraction coatings (ARCs) of solar cells is introduced. The nanostructure ARCs are generated by O\textsubscript{2} Plasma surface modification technique for a flexible polydimethylsiloxane (PDMS) polymeric film, the microstructure ARCs are obtained by soft imprint lithography, and the micro-nano complex structure PDMS ARCs are fabricated by soft imprint lithography technique combined with surface modification technique. The measured results show that these PDMS ARCs can decrease reflection loss of light from the solar cells and increase the solar cells photovoltaic conversion efficiency.

1. Introduction
Solar cells made out of the crystalline or amorphous silicon wafer are most widely used in the photovoltaic industry with comparatively low cost and relatively high efficiencies to convert the solar energy into the electric energy. Since micro/nanostructures have a broadband and omnidirectional light-harvesting capability, various micro and nano structures arrays, for example, nanometer-sized demes array [1], micro/nanocones array [2], micro/nanopyramids array [3], nanowire and nanopillars array [4] and nanospheres array [5], and so forth, have been extensively studied to reduce the reflection loss from solar cells and strengthen the light capturing in photovoltaic (PV) active materials. On the other hand, to protect the solar cell from the inclemencies of the weather, particles of dust, etc., Solar cells need to be packaged. However, the simple and flat package surface will degrade the antireflection property of micro-nano structure on the silicon surface of solar cell [6].

The surface texturing antirefraction coatings (ARCs) on the surface of coverglass package or thermal epoxy resin film can redirect as much of the incident energy as possible into the solar cell and Increase the omni-directional angle and broadband optical capture capability of solar cells. Hence, a variety of ARCs with surface textures have been extensively applied to reduce the reflection loss of solar cells [7-9].

We introduce our research group’s recent progress in low-cost fabrication of micro-and nano-structured PDMS ARCs for solar cells in this report. The micro-nano complex structure polydimethylsiloxane (PDMS) ARCs are fabricated by soft imprint lithography technique combined with surface modification technique. The measured results show that these PDMS ARCs can effectively reduce light reflection loss of solar cells and substantially enhance the photovoltaic conversion efficiency (PCE) of silicon solar cells devices.
2. Experiments and Results

2.1. Nanowrinkle Structure PDMS ARC [10]

Surface modification of PDMS thin films by oxygen plasma resulted in the formation of nanowrinkling structure on PDMS film surface. Figure 1 shows the fabrication procedure of a nanowrinkle structure PDMS ARC of solar cells. The atomic force microscope (AFM) images of wrinkle structure at different plasma exposure time of t=60s and t=90s was shown in figures 2a and 2b. It was can be seen that the wrinkle periods at exposure time of t=60s and t=90s are obviously different. To analyse the relationship between the wrinkle structure and the plasma exposure time, figures 2c and 2d showed influence of the plasma exposure time on the wrinkle structure (wrinkle period in space and aspect ratio of wrinkle). It can be seen that period and depth of wrinkles exhibited linearly dependence on plasma exposure time while the aspect ratio of the wrinkle AR film kept constant when the plasma exposure time was longer to 90s. The indications were explained that the chemical reaction under plasma caused a build-up of the top rigid layer. As the chemical reaction proceeded, the density of the thin layer on the surface of the PDMS film was increased from pure PDMS elastomer to the resultant value of the modified thin layer on the FDMS’s surface. For a short exposure time, the density and stiffness of the top layer were low. The aspect ratio increased with increase of the plasma exposure time. Nevertheless, the density of the top layer approached to a constant for a long exposure time, as shown by the plateau in aspect ratio.

In our experiment, a low-elastic-modulus PDMS slab was stretched to 20% and of which area and height are 40 mm × 90 mm and 1.5 mm, respectively. The work electrode power of the inductively coupled high density plasma device (ICP) were set 200 W and and its vacuum were pumped 5×10⁻³ Pa. Then the reaction cavity in ICP device was inflated with O₂ gas of 1 sccm rate of flow and kept 0.5Pa pressure throughout the process. Under plasma, a rigid layer on the pre-stretched PDMS slab was created by chemical reaction between air and PDMS. And removing the applied mechanical strain, the rigid layer at the surface of the PDMS slab was buckled and the self-assemble wrinkle can be formed. The AFM images of PDMS wrinkle structure at different plasma exposure time of t=60s and t=90s was shown in figures 2a and 2b. It was can be seen that the wrinkle periods at exposure time of t=60s and t=90s were obviously different. The period difference of wrinkles was attributed to the change of elastic modulus of the rigid layer under different O₂ plasma exposure time.

The purpose of introducing the wrinkled PDMS AR film is to enhance conversion efficiency of the crystalline solar cell and its hydrophobicity. Figures 3a-3c show the current-voltage curves of silicon-wafer solar cells with and without wrinkles which provided direct evidence of the AR effect measured by the use of the Newport Oriel PVIV–201V IV Station under 1 Sun illumination (AM1.5). The PCEs of the crystalline solar cells with and without wrinkles were obtained under three different incidence angles of θ=0°, θ=30° and θ=60°. It is founded that 1.2%, 8.1% and 43.1% enhancement of conversion efficiency is achieved and the larger the incident angle, the more efficiency improvement. These observations suggest that the enhancement of the crystalline solar cell efficiency is not obvious at normal incidence, while the efficiency was pronouncedly increased with a high incidence angle. In order to explain the enhancement of the conversion efficiency, the Reflection spectrum spectra of the crystalline solar cell devices with and without wrinkling ARCs under the different incident angles were calculated as shown in figure 3d. The reflectivity of the crystalline solar cell with and without wrinkles were increased with the increase of the incident angle in the range from 0° to 60°. However, the reflection difference became increasingly remarkable with amplification of the incident angle.

2.2. High Aspect Ratio Microlens Array Structure PDMS ARC

Figure 4 schematically shows the procedure of preparing close-packed and high aspect-ratio paraboloidal microlens array (PMLA) ARCs [11]. Figure 5a shows scanning electron microscopy (SEM) images of PMLAs. The photoresist molds were fabricated by using the UV laser-writing system under different exposure powers varied from 14 mW to 24 mW. And then the photoresist mold pattern was duplicated to PDMS film. The SEM images shows that the geometric morphology fabricated the microlens array is in a paraboloid shape. It is obviously found from figure 5 that the larger the exposure
powers, the higher the microlens. But the width of microlens keeps basically unchanged in the beginning stage of increasing exposure power and then gradually increases its maximum value of 7 μm at 24 mW. In the range of 14-24 mW exposure powers, however, the height of PMLAs keeps increasing, reaching to its maximum value of about 7.4 μm at 24 mW. These interesting phenomena is explained in Ref. [4, 12].

Figure 1. Fabrication procedure of a solar-cell antireflective coating of PDMS with an ordered wrinkle. (a) A PDMS film was formed by mixed a prepolymer and a curing agent with a weight ratio of 10: 1 and then degassed in the vacuum drying oven and baked at 80˚C for 8 hours. (b) The PDMS film was stretched and put into ICP etching device. (c) The PDMS surface was modified by plasma treatment and an oxidized thin layer was come into being on the PDMS film surface. (d) Nanowrinkle structure in the top of the PDMS film after the pre-stress was released. (e) The PDMS with the ordered wrinkle was attached to the commercial silicon-wafer solar cell panel without any adhesive agent. (f) A photograph of solar cell device with a nanowrinkle PDMS ARC in sunlight.

Figure 2. AFM images of PDMS wrinkle structure at different plasma exposure time with same stretch, (c) period and depth as well as (d) aspect ratio of wrinkles versus exposure time.
Figure 3. Current-voltage (I-V) curves of PV devices with and without wrinkle PDMS film measured under several incidence angles of (a) $\theta = 0^\circ$, (b) $\theta = 30^\circ$ and (c) $\theta = 60^\circ$, (d) Reflectance spectra of crystalline solar cell with and without wrinkle PDMS film versus incidence angle.

Figure 4. Fabrication process of PMLA-structure PDMS ARC: (a) Photoresist film exposure by UV laser photolithography, (b) The photoresist template after developed, (c) Premixed PDMS poured on photoresist template, (d) Paraboloidal PDMS microlens array after peeling off from the photoresist template.

The electrical properties of silicon-wafer solar cells with and without a PDMS PMLA ARC. Figure 6a shows the measured $J$-$V$ curves of the device measured under 1 Sun illumination, where the red curve is the case with a flat PDMS film and the black curve is the case with the fabricated PMLA PDMS ARC.
whose structure was fabricated under 24 mW exposure power. Table 1 (the insert in figure 6a) shows measurement results of several main electrical parameters including the open-circuit voltage $V_{oc}$, short-circuit current density $J_{sc}$, filled factor $FF$, and photovoltaic conversion efficiency $PCE$. It is found that the $J_{sc}$ of the device increases from 37.2 with a flat PDMS film to 35.6 mA/cm$^2$ with the PMLA PDMS ARC. $J_{sc}$ being improved 4.5%. Both $V_{oc}$ and $FF$ have a negligible change. It is known that the PCE is proportional to the product of $J_{sc}$, $V_{oc}$ and $FF$. It can be calculated from the values in table 1 that the PCE of the solar cell is increased from 16.7% to 17.7%, that is, the PMLA ARC improves the solar cell absolute PCE by 1%.

**Figure 5.** The SEM images of fabricated PDMS MLAs where the photoresist templates were lithographed under different exposure energy of (a) 14, (b) 15, (c) 16, (d) 20, (e) 22 and (f) 24 mW. Inset: SEM images taken when the sample is tilted 60 degrees. Scale bar length represents 10 μm.

**Figure 6.** (a) $J$-$V$ curves of silicon-wafer solar cells with and without PMLA ARC under normal incidence of AM1.5G. Inset Table 1: performance parameters of the solar cells. (b) PCEs versus the incident angle of simulating AM1.5G, where the black curve is the relative PCE improvement of the solar cell with the PDMS PMLA ARC compared with a flat PDMS film.

Figure 6b shows the dependence of measured silicon-wafer solar cell PCE on the incident angle which varies 0° (normal incidence) to 60° with an interval of 10°. Although the PCEs dramatically reduce as the incident angle increases, the PCE with the PDMS PMLA ARC is always higher than that with a flat PDMS coating in the whole range of incident angles and the PCE improvement increases
with increasing incident angle. Numerical results show that compared with the solar cell with the flat PDMS coating, the PCE with the PDMS PMLA ARC is higher than about 5.6% at each incident angle and the average increment percentage value is about 10.9% over the 0-60° incident angle angles.

2.3. Affiliations Submillimeter-Nanometer Multiscale Array ARCs [13]
Submillimeter-nano multiscale array (MSA) light-trapping structures were successfully demonstrated on a flexible PDMS polymeric film by simple injection molding combined with surface modification technique. Figure 7 illustrates the process to fabricate the MSA structures, where the submillimeter array glass template consists of 200μm diameter glass rods glued together tightly side by side. The pattern of the glass template was duplicated onto the PDMS film by soft imprint method. Applied the surface modification method in the 2.1 section above, the nanowrinkle surface was formed along the axial direction of the submillimeter concave cylinders (CCA).

Figure 7. Fabrication procedure of MSA structures. (a) A CCA PDMS film peeled off from the glass template. (b) Pre-stretching the PDMS film along the axial direction of CCA. (c) Surface modification by O₂ plasma exposure in ICP device. (d) Silane thermal evaporation treatment. (e) MSA PDMS ARC coated on silicon solar cell.

Figure 8. SEM images of the fabricated PDMS ARC with a surface of submilli-nano complexed structures.

In order to clearly compare AR properties with different structures, the multiple scale, single submilli-scale CCA and single nano-scale wrinkle PDMS ARCs (figure 8) were respectively used to install on the surface of the same epoxy resin polymer (ERP) film which encapsulates silicon-wafer solar cells. It is worth noting that the nanowrinkle’s aspect ratio and period on the surface of the 200 μm-in-diameter CCA are 0.263 and 658 nm which manufactured under t=60s and εpre=25%. Figure 9 shows the reflective spectrum of an ERP-encapsulated silicon solar cells without any ARC and with a PDMS single-submilli-scale CCA, single-nanoscale wrinkle and multiscale MSA PDMS ARC, respectively. It can be simulated by using the finite difference time domain method (FDTD) that the integrated reflectivity of the ERP-encapsulated silicon-wafer solar cell over the 300~1100 nm wavelength range are 7.63%. the PDMS ARC can reduce reflectivity to 3.78% for the multiscale MSA.
structure, 5.17% for the single-submilliscale CCA structure and 5.74% for the single-nanoscale wrinkle structure, respectively.

The electrical properties of the ERP-encapsulated silicon solar cell with different AR structure were thoroughly measured. Figure 10 shows that $J-V$ curves of the ERP-encapsulated silicon-wafer solar cells with different ARCs. The PCEs of the ERP-encapsulated silicon solar cell is 17.50% without any ARCs. When the multiscale MSA PDMS ARC is used, the PCE of the device is improved to 17.92%. By contrast, the PCE of the device is improved only to 17.81% using the single-submilliscale CCA PDMS ARC and to 18.21% using the single-nanoscale wrinkle PDMS ARC, respectively. These results imply that the multiscale MSA PDMS ARC is superior to the two single-scale PDMS ARCs in improving the solar cell PCE.

![Figure 9](image1.png)

**Figure 9.** Reflective spectrum of the ERP-encapsulated silicon-wafer with different ARCs. The period and aspect ratio of PDMS nanowrinkle are $P=658$ nm and $\gamma=0.263$ respectively in the multiscale MSA and singlescale wrinkle PDMS films.

![Figure 10](image2.png)

**Figure 10.** Measured current density and voltage ($J-V$) curves for the solar cell with different ARCs under 1 Sun normal incidence of AM1.5G. The PDMS nanowrinkle structure is fabricated under the conditions of 60 s plasma exposure time and 25% pre-stretching rate.

## 3. Conclusion

In conclusion, we have confirmed some facile process to manufacture flexible submilliscale, microscale, nanoscale, and submilli-nano multiscale PDMS ARCs with economical and well-designed method. These PDMS ARCs can be easy mounted on silicon-wafer solar cells. The optical and electrical property measurements have shown that these PDMS ARCs can decrease the reflection loss on the front surface and improve the conversion efficiency of silicon-wafer solar cells. By comparison, the effect of
multiscale array structure ARCs is better than that of single microarray structure and single nano array structure ARCs in improving solar cell efficiency and reducing light reflection loss. In general, the process of fabrication proposed here is simple and universal and it enables a new method to fabricate cheap ARCs for PV applications.

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