Reusable Moth-Eye nano-patterned PDMS sticker with a versatile function of coating for photovoltaics.

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ABSTRACT

A multifunctional polymer films, capable of reducing reflections of incident light on the photovoltaic surface, were developed. Taking advantage of polydimethylsiloxane (PDMS) properties which are not only smoothly adhered to flexible substrates but easily controlled in morphology as well, we fabricated sticker-like film with moth-eye nano-patterns on the PDMS surface. As shown in Figure 1, with simple attachment of the developed film to Si solar cell, we showed that the short circuit current density and power conversion efficiency of the solar cell increased by up to 0.8mA/cm^2 and 0.4 percentage points in absolute values, respectively. As anti-reflective stickers, the developed films are versatile in application for various fields such as light-emitting diodes, surface-emitting lasers, camera lens, etc and expected to aid in overcoming limits of material absorption and device structures.

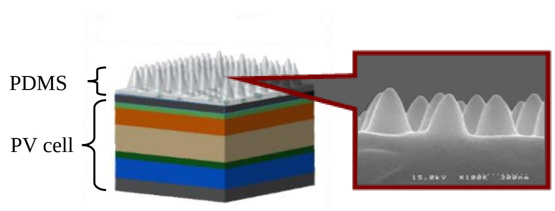

Figure 1: The schematic view of moth-eye nano-patterned PDMS sticker-attached photovoltaic cell and the SEM image of 0.42μm diameter polystyrene(PS) bead-patterned PDMS.

Keywords: photovoltaics, anti-reflective, sticker, nano-pattern, polydimethylsiloxane

1 INTRODUCTION

In solar photovoltaic systems, enhancing absorption of the incident light on the device surface through reducing reflection is crucial for improving the system performance. In the traditional layered method for anti-reflective coatings (ARCs), however, there are not a few limitations in achieving ARCs, because it depends on the wavelength, angle, and polarization of the incident light.[1-3] Thus, only under the specific conditions the traditional layered ARCs are available, rendering it hard to practially utilize the traditional layered ARCs. On the contrary, the bio-inspired nanostructures provide amazing multifunctional properties as well as those overcoming the limitations of the traditional layered ARCs, e.g. broadband and quasi-omnidirectional antireflection, hydrophilicity-based antifogging, and superhydrophobicity-based self-cleaning in combination with optical, mechanical, and adhesion properties.[4-10] When it comes to anti-reflective properties, especially moth-eye nanostructures exhibit exceptional broadband and wide-angle performances compared to the conventional ARCs, anticipating the moth-eye nanostructures in practical use as ARCs.[11-14] Actually in various fields of camera lens, light-emitting diodes, surface-emitting lasers, flat panel displays, photodetectors, solar cells and so on, moth-eye nanostructures have been employed as powerful ARCs for devices' performances such as sensitivity, accuracy and efficiency enhancement.[15-20]

In the present work, using thre most common silicon-based organic polymer, i.e. polydimethylsiloxane (PDMS) with such advantageous material properties to this concept as easily controllable morphology, adherence to the flexible substrate, ease of large-area fabrication and so on, moth-eye nano-patterned ARCs which are protuberant, aspect ratio >1 long and truncated corn-like shape are fabricated for both the photovoltaic performance enhancement and the device surface protection. Here, the nanostructured PDMS sticker was replicated by soft imprint lithography using Si master prepared thorugh self-assembly lithography with three different sizes of polysterene (PS) beads.

There are two novelties in this work. The first, the moth-eye nano-patterned PDMS ARCs of this work are in contrast with the previously reported ARCs[21-34], which are fixed in the device itself through patterning the device or the ancillary process such as encapsulation[35], in that the developed films of this work are free from the device just like a sticker with ability both repeatedly attachable and easily detachable even to any kind of device shape. Even more, this sticker needs no additional adhesives when applied to photovoltaics. Thus can be applied not only to various types of photovoltaic devices in their as-fabricated conditions, but, taking into account the manufacturing capability of large-area films, to the cover glass of conventional crystalline Si solar modules. And the second, it is state of the art to make the protuberantly nano-patterned PDMS with high aspect ratio (>1), taking into account the fabrication difficulty attributed to PDMS nanosturcture's collapse and clustering while hollw patterns on PDMS are well researched. We have confirmed the novel PDMS film effect to photovoltaics and its characteristics as powerful ARCs analyzing reflectance in the wide range of wavelengh from near-UV through visible to near-IR, the short circuit current density and power conversion efficiency of photovotaics. The PDMS film of this work, as an easy-to-use sticker, is expected widely applicable thus useful to such devices as flat panel displays, photodetectors, photovoltaics, etc.

2 RESULTS AND DISCUSSION

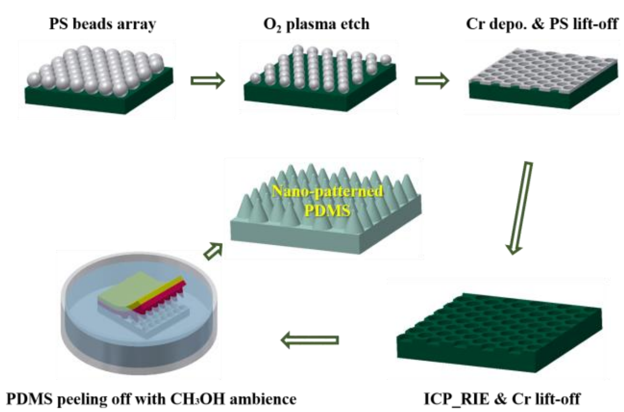

Figure 2: The schematic view of fabrication process of moth-eye nano-patterned PDMS sticker.

Nano-patterned Si mold was fabricated by self-assembly, deposition, and dry etching processes. With the Si mold, biomimetic moth-eye-like PDMS film could be achieved through soft imprinting lithography. Figure 2 shows the whole schematic fabrication process. When it comes to PDMS, two kinds of products were advertently selected, i.e. soft PDMS(s-PDMS) for easy control of the fabricated film and hard PDMS(h-PDMS) for high nano-pattern quality, constituting double layers both of the s-PDMS bottom layer that is the most part of the fabricated film and of the h-PDMS surface layer, the nano-pattern part. A delicate process is strongly required in making such PDMS nano-pattern as protuberant and aspect ratio >1 long(1.38 in this work), due fabrication difficulty attributed to PDMS nanostructures' collapse and clustering. Not being overcome only by h-PDMS alone for high nano-pattern quality, the common and frequent fabrication failure could be notably and innovatively beaten through peeling off the pattern from the mold with methyl alchol(CH_3OH) ambience.

The developed PDMS films were different one another in nano-pattern size, fabricated with three different sizes of 0.99µm, 0.57µm, and 0.42µm diameter, Chloromethyl latex polysterene (PS) beads. Both the different PDMS films and the related Si molds by which those PDMS films were respectively imprinted are shown in Figure 3. And a single junction a-Si:H solar cell layering sequently with Al metal, back reflector, P-I-N, front TCO and glass was utilized for evaluation of ARCs effect to power conversion efficiency. Figure 1 shows both the graphic and scannig electron microscope(SEM) images of PDMS film-attached a-Si:H solar cell.

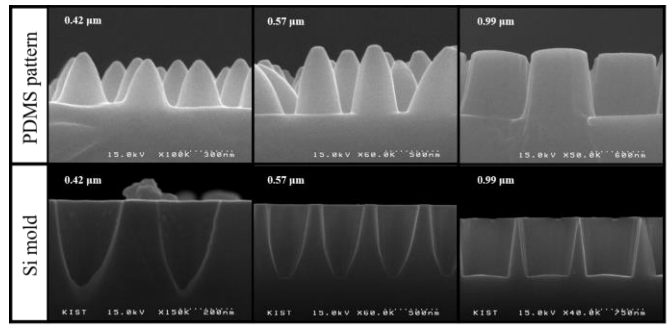

Figure 3: The SEM images of 0.42µm, 0.57µm, 0.99µm polystyrene(PS) bead-patterned Si molds and PDMS films.

By Figure 4 and Table 1, we are convinced the fact that all of three different PDMS films improved PV performance. In the performance enhancement point of view, we can rank the films in the sequence of, from the highest to the lowest, 0.57µm diameter PS-patterned PDMS(0.57) > 0.42µm diameter PS-patterned PDMS(0.42) > 0.99µm diameter PS-patterned PDMS(0.99) as well. In comparison with the short circuit current density(J_{sc}) and the efficiency of the reference cell, 0.99 increased them by 0.4mA/cm^2 and 0.2%, 0.42 increased by 0.6mA/cm^2 and 0.3%, and 0.57 increased by 0.8mA/cm^2 and 0.4%, respectively. We can also see at Table 1 that there were no fluctuations in open circuit voltage(V_{oc}) and Fill Factor(F.F), which means there were no significant changes in other conditions such as semiconductor material properties, device resistance, etc. The electrical properties of PV were measured under 100mW/cm^2, AM 1.5G, 1-SUN with XES-301s xenon lamp(SAN-EI ELECTRIC Co., Ltd.), XEC-301s lamp controller (SAN-EI ELECTRIC Co., Ltd.), and SMU 2400 source meter(Keithley instruments, Inc.). Figure 5 shows that these enhancements of PV performance are ascribed to moth-eye nano-patterns' anti-reflection effect.

	Voc (V)	Jsc (mA/cm²)	Fill Factor	Efficiency (%)
Ref	0.855	15.787	70.14274	9.4656
0.42PS	0.854	16.355	69.92079	9.7648
0.57PS	0.855	16.553	69.72675	9.8736
0.99PS	0.855	16.15	69.91831	9.656

Table 1: The electrical properties of the single junction a-Si:H solar cell w/ or w/o moth-eye nano-patterned PDMS film.

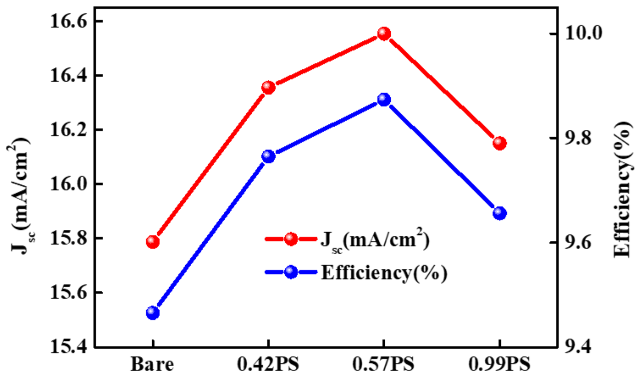

Figure 4: Short circuit current density(J_{sc}) and efficiency of the single junction a-Si:H solar cell w/ or w/o moth-eye nano-patterned PDMS film.

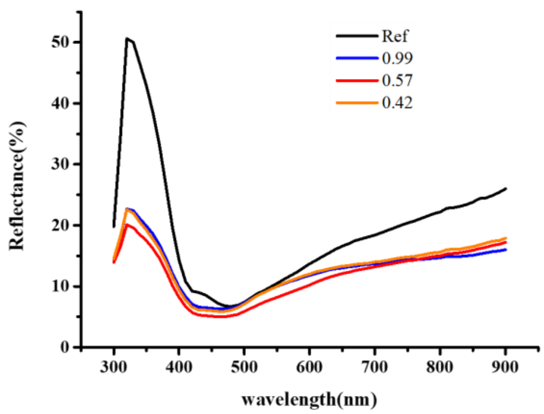

Figure 5: Reflectance of reference cell w/ or w/o moth-eye nano-patterned PDMS film.

3 EXPERIMENTAL SECTION

3.1 Nano-patterned Si mold fabrication

Boron-doped, 275±15µm thickness, 2 inch diameter, p type, 1-10 resistivity and 1-0-0 orientation Si wafer(Waferbiz, Inc.) was diced into 1cm by 1cm dimensions to be the mold base substrate before self-assmebly, deposition and dry etching processes. And 0.99µm, 0.57µm, and 0.42µm diameter, 4% w/v, Chloromethyl latex polystyrene(PS) bead(CureBio, Inc.) was diluted 1:1 with ethyl alcohol and then used in the self-assembly step as a deposition mask, achieving the compact PS monolayer on the diced Si substrate through Langmuir Blodgett method. The deposition and dry etching processes are as follows that firstly we shrank PS bead size to the extent in which the filling ratio(reduced diameter over pitch in this work) became about 60% varying etching time with 70sccm O2 flow in the inductively coupled plasma(ICP) etcher(Oxford-instruments Inc.), secondly covered the exposed Si surface among shrunk PS beads with 100nm Cr deposition by e-beam evaporator(ULVAC Inc.) in order to keep the selective Si surface from etching, then rinsed PS bead with $CHCl_3$, thirdly etched Cr-coated Si substrate with the gases of both Ar and Cl_2 during 200 seconds through ICP etcher(Oxford-instrument Inc.) to dig the blunt corn-like shape of nano-holes on Si substrate, fourthly eliminated Cr mask using $(NH_4)_2Ce(NO_3)_6$+$HN)_3$ Cr etchant, and finally coated polytetrafluoroethylene(PTFE), so called Teflon, on the nano-patterned Si mold as an anti-adherent layer for easy peelilng off PDMS from the mold.

3.2 Nano-patterned PDMS film fabrication

0.5g of Vinylmethysiloxane-Dimethylsiloxane Copolymers Trimethylsiloxy terminated VDT-731 was mixed with 2.648µℓ of Platinum-divinyltetramethyl-disiloxane complex in xylene SIP6831.2LC and stirred for 30 seconds. And then, 17.645mg of 1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane SIT7900.0 was added to the mixture and stirred again for 30 seconds. 0.145g of Methylhydrosiloxane-Dimethylsiloxane Copolymers Trimethylsiloxy terminated HMS-301 (Gelest, Inc.) was lastly complemented and stirred for 30 seconds to be the h-PDMS compound. After extracting bubbles out of the h-PDMS compound in the vaccum chamber, 100µℓ of the compound was coated on the nano-patterned Si mold by AC-200 spin coater(DONG AH Trade Corp.) with the conditions of 6000rpm, 6 minutes. And then, the coated mold baked at 60°C for 30 minutes on the hot plate to be 1.5~2µm thick. Meanwhile, 1mℓ of Sylgard 184 silicon elastomer base was mingled with 100µℓ of Sylgard 184 curing agent (Dow Corning Co.) to be the s-PDMS compound. Eradicating bubbles from the s-PDMS compound in vaccum chamber was followed by that 100µℓ of the compound was cast over the precedently cured cured h-PDMS-coated Si mold and spun with the speed of 1000rpm for 30 seconds. And the mold baked at 90°C for 1 hour to be about 100µm thick. We peeled off the h/s-PDMS film from the mold while submerging the mold into methyl alcohol in order to avoid PDMS nano-patterns' collapse and clustering.

4 CONCLUSION

In this work, we developed the multi-functional polymer films, which are like a sticker and capable of anti-reflection of incidence as well as surface protection of photovoltaics, with the moth-eye nano-patterns on the surface. With a simple attachment, attributed to sticker-like characteristic, of the developed film on the photovoltaics we achieved performance enhancement in short circuit current density(J_{sc}) and efficiency by upto 0.8mA/cm^2 and 0.4 percentage points in absolute values, respectively. As a powerful and ease-to-control ARCs, the developed films are expected applicable to various fields such as light-emitting diodes, camer lens, photodetectors and so on.

5 ACKNOWLEDGEMENT

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REFERENCES

[1] S. Chattopadhyay, Y. F. Huang, Y. J. Jen, A. Ganguly, K. H. Chen, and L.C. Chen : Materials Science and Engineering, R, 2010, 69, 1-35.

[2] Jinguang Cai and Limin Qi : mater. Horiz., 2015, 2, 37-53.

[3] H. K. Raut, V. A. Ganesh, A. S. Nair, and S. Ramakrishna : Energy Environ. Sci., 2011, 4, 3779-3804.

[4] K. Park, H. J. Choi, C. Chang, R. E. Cohen, G. H. McKinley, G. Barbastathis : ACS Nano, 2012, 6, 3789-3799.

[5] H. Lim, D. H. Jung, J. H. Noh, G. R. Choi, W. D. Kim : Chin. Sci. Bull., 2009, 54, 3613-3616.

[6] Y. Zheng, X. Gao, L. Jiang : Soft Matter, 2007, 3, 178-182.

[7] D. Y. Lee, D. H. Lee, S. G. Lee, K. Cho : Soft Matter, 2012, 8, 4905-4910.

[8] Y. Li, J. Zhang, S. Zhu, H. Dong, F. Jia, Z. Wang, Z. Sun, L. Zhang, Y. Li, H. Li, W. Xu, B. Yang : Adv. Mater., 2009, 21, 4731-4734.

[9] K. M. Wisdom, J. A. Watson, X. Qua, F. Liu, G. S. Watson, C. H. Chen : Proc. Natl. Acad. Sci. U.S.A., 2013, 110, 7992-7997.

[10] J. W. Leem, J. S. Yu : Opt. Express, 2012, 20, 26160-26166.

[11] D. G. Stavenga, S. Foletti, G. Palasantzas, K. Arikawa : Proc. R. Soc. London, Ser., 2006, B, 273, 661-667.

[12] B. Paivanranta, T. Saastamoinen, M. Kuittinen : Nanotechnology, 2009, 20, 375301.

[13] Y. F. Huang, S. Chattopadhyay, Y. J. Jen, C. Y. Peng, T. A. Liu, Y. K. Hsu, C. L. Pan, H. C. Lo, C. H. Hsu, Y. H. Chang, C. S. Lee, K. H. Chen, L. C. Chen : Nat. Nanotechnol., 2007, 2, 770-774.

[14] C. H. Sun, P. Jiang, B. Jiang : Appl. Phys. Lett., 2008, 92, 061112.

[15] T. Taguchi, H. Hayashi, A. Fujii, K. Tsuda, N. Yamada, K. Minoura, A. Isurugi, I. Ihara, Y. Itoh : SID Int. Symp. Dig. Tech. Pap., 2010, 41, 1196-1199.

[16] J. Zhu, C. M. Hsu, Z. Yu, S. Fan and Yi Cui : Nano Lett., 2010, 10, 1979-1984.

[17] J. Zhang, S. Shen, X. X. Dong and L. S. Chen : Opt. Express, 2014, 22, 1842.

[18] Y. He, W. Zhang, S. Zhang, X. Kang, W. Peng and Y. Xu : Sens. Actuators, A, 2012, 181, 6.

[19] N. Yamada, T. Ijiro, E. Okamoto, K. Hayashi and H. Masuda : Opt. Express, 2011, 19, A118-A125.

[20] T. Song, S. T. Lee and B. Sun : Nano Energy, 2012, 1, 654.

[21] S. G. Lee, D. Y. Lee, H. S. Lim, D. H. Lee, S. Lee and K. Cho : Adv. Mater., 2010, 22, 5013.

[22] J. Li, J. Zhu and X. Gao : Small, 2014, 10, 2578.

[23] S. H. Lee, J. W. Leem and J. S. Yu : Opt. Express, 2013, 21, 29298.

[24] F. Wu, G. Shi, H. Xu, L. Liu, Y. Wang, D. Qi and N. Lu : ACS Appl. Mater. Interfaces, 2013, 5, 12799.

[25] J. W. Leem, J. S. Yu, J. Heo, W. K. Park, J. H. Park, W. J. Cho and D. E. Kim : Sol. Energy Mater. Sol. Cells, 2014, 120, 555-560.

[26] F. Galeotti, F. Trespidi, G. Timo and M. Pasini, *ACS Appl. Mater. Interfaces*, 2014, 6, 5827.

[27] H. K. Raut, S. S. Dinachali, A. Y. He, V. A. Ganesh, M. S. M. Saifullah, J. Law and S. Ramakrishna, *Energy Environ. Sci.*, 2013, 6, 1929.

[28] X. Zhang, D. Ji, T. Lei, B. Zhao, K. Song, W. Hu, J. Y. Wang, J. Pei and Y. Wang, *J. Mater. Chem. A*, 2013, 1, 10607.

[29] S. Y. Chuang, C. C. Yu, H. L. Chen, W. F. Su and C. W. Chen, *Sol. Energy Mater. Sol. Cells*, 2011, 95, 2141.

[30] K. Choi, S. H. Park, Y. M. Song, Y. T. Lee, C. K. Hwangbo, H. Yang and H. S. Lee, *Adv. Mater.*, 2010, 22, 3713.

[31] J. K. Hyun, C. Ahn, H. Kang, H. J. Kim, J. Park, K. H. Kim, C. W. Ahn, B. J. Kim and S. Jeon, *Small*, 2013, 9, 369.

[32] K. Forberich, G. Dennler, M. C. Scharber, K. Hingerl, T. Fromherz and C. J. Brabec, *Thin Solid Films.*, 2008, 516, 7167.

[33] K. Choi, S. H. Park, Y. M. Song, C. Cho and H. S. Lee, *J. Mater. Chem.*, 2012, 22, 17037.

[34] D. H. Ko, J. R. Tumbleston, K. J. Henderson, L. E. Euliss, J. M. DeSimone, R. Lopez and E. T. Samulski, *Soft Matter*, 2011, 7, 6404.

[35] J. W. Leem, S. Kim, S. H. Lee, J. A. Rogers, E. Kim and J. S. Yu, *Adv. Energy Mater.*, 2014, 4, 1301315.