Science and Innovation of Advanced Materials

The Materials Research Society of Thailand

Research Article

Efficient Four-Terminal Perovskite/Silicon Tandem Solar Cells by Using an Anti-Reflective Polymer Film as an Intermediate Matching Layer

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Received: *May 17th, 2023* | ***Revised:*** *June 29th, 2023* | ***Accepted:*** *June 29th, 2023*

Abstract: Perovskite/silicon tandem solar cell is a promising candidate for highly efficient photovoltaic technologies. The 4T perovskite/silicon tandem solar cell comprises individual sub-cells that require no current matching. However, an optical loss to the bottom cell is a major issue, which is caused by an air gap serving as an optical spacer layer between sub-cells. This air gap results in a reduction in performance. In this work, commercial polydimethylsiloxane (PDMS) [Sylgard®184] was used as an intermediate matching layer (IML) in the 4T perovskite/silicon tandem cells to eliminate the air-spacer layer and increase the efficient performance. The PDMS anti-reflective polymer film was sandwiched between the top and bottom cells. The process has the potential to significantly improve the current density of silicon bottom cell with an active area of ~0.96 cm^2 from 13.39 mA/cm^2 (without an IML) to 14.95 mA/cm^2 (with an IML). The calculating overall performance of 4T perovskite/silicon heterojunction tandem cells with an air gap and an IML were achieved a *PCE* of 20.77% and 21.57%, respectively.

Keywords: Air-spacer layer, Anti-reflective polymer film, Perovskite/silicon tandem solar cells, Polydimethyl-siloxane

1. Introduction

Perovskite/silicon tandem solar cell have attracted significant attention due to their highly efficient performance, surpassing the physical limits of conventional silicon solar cell technologies [1-3]. There are two main configurations of tandem solar cells; monolithically integrated two-terminal (2T), and mechanically stacked four-terminal (4T) tandems. To harvest all wavelength of light, the wide energy band gap perovskite and narrow band gap silicon are used as the top and bottom cells, respectively [4,5]. To achieve high efficiencies in the tandem design, the perovskite solar cell (PSC) with transparent electrodes harvests light at short wavelengths, while the silicon bottom cell

* Presented at The 4th Materials Research Society of Thailand International Conference

absorbs the long wavelength light. Currently, the 4T perovskite/silicon tandem solar cells have reported the highest power conversion efficiency (*PCE*) in exceed of 30% [6]. The advantage of the 4T perovskite/silicon tandem solar cell is that they are connected in series by individual sub-cells without the need for current or voltage matching. Only optical coupling of the sub-cell is required to induce light to pass through tandem devices, Perovskite top cells with a transparent electrode are essential for optical optimization.

When considering the optical loss to the bottom cell, the inclusion of an air gap or an optical spacer layer between sub-cells have been shown to reduce the performance of solar cell [7]. In order to improve the performance of 4T tandem devices, it is necessary to eliminate the air gap. To achieve this, an intermediate matching layer (IML) has been developed as a substitute for the air-spacer layer, resulting in improved 4T perovskite/silicon tandem cell efficiencies [8]. The IML, when coated with an anti-reflective material, is able to minimize optical losses. PDMS is particularly interesting alternative material for the IML due to its high transparency, excellent hydrophobicity, suitable reflective index value, and simple processing [9,10].

In this study, we investigated the use of PDMS, specifically commercial-PDMS (Sylgard®184), as an IML in the 4T perovskite/silicon tandem cells. Our goal was to eliminate the air-spacer layer and enhance the performance of device. The optical properties of PDMS films were investigated. The first experiment, the performance of standard silicon bottom cell filtered with different models made of two glasses without and with the PDMS layer, refer to as glass/air gap/glass and glass/PDMS/glass, respectively was measured. Then, 4-terminal perovskite/silicon tandem solar cells composed of semitransparent perovskite top cell and silicon heterojunction bottom cells with an air gap and an IML was carried out. The current density of silicon bottom devices is significantly enhanced from 13.39 mA/cm^2 (with an air gap) up to 14.95 mA/cm^2 (with an IML). Consequently, the total *PCE* of 4T PSC/silicon tandem without an IML is 20.77%, while the cell with an IML demonstrated the highest efficiency of 21.57%.

2. Methodology

Preparation of PDMS film

Commercial PDMS materials (Sylgard®184) was supplied by Dow Corning Co. The PDMS solution was conducted by a mixture of a base polymer resin and a curing agent with a weight ratio of 10:1. For preliminary study the effect of an IML for silicon bottom cell performance, the PDMS layer sandwiched between the glasses was stacked on the silicon bottom cells compare to an air gap sandwiched between the glasses. PDMS was drop-cast on a glass surface and was placed by another glass. To fabricate completely 4T perovskite/silicon tandem devices with an IML, the preparation of PDMS was poured on the top of the surface of silicon solar cells and then stacked a semitransparent perovskite top cell. The fully tandem devices were kept at room temperature for over 24 hours to obtain fully cross-linked PDMS. The PDMS layer as an IML was coated on a bare-glass substrate to characterize the optical properties.

Fabrication of perovskite and silicon solar cells

A one-step method was used for the fabrication of semitransparent perovskite solar cells as a top cell corresponding with glass/ITO/SnO_2/triple-cation perovskite ($Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$)/spiro-OMeTAD/ITO configuration. For the SnO_2 as an electron transporting layer (ETL), 3%wt SnO_2 nanoparticles was dispersed in deionize water, following by stirring at room temperature for 60 min. The obtained SnO_2 solution was coated on the cleaned ITO glass substrates by a spinning technique at 4000 rpm for 20 s and then heated at 110 °C for 30 min. To prepare the triple-cation perovskite solution, the mixture of 1.0 M formamidinium iodide (FAI), 0.2 M methylammonium bromide (MABr), 1.1 M lead iodide (PbI_2), and 0.2 M lead bromide ($PbBr_2$) was disolved in the mixed solvent of dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) with a volume ration of 4:1. The solution was stirred at 100 °C for 60 min and then cesium iodide (CsI) solution was added in the perovskite precursor. The perovskite solution was spin-coated directly on the SnO_2 film at 3000 rpm for 30 s. Chlorobenzene (250 μl) was dropped on the perovskite 25 s after starting the spinning time. The perovskite film was heated at 100 °C for 30 min. The spiro-OMeTAD as a hole transporting layer (HTL) was prepared by dissolving 72.3 mg of the spiro-MeOTAD in 1 mL chlorobenzene, following 28.8 μL of 4-tert-butylpyridine and 17.5 μL of Li-TFSI stock (520 mg/mL in acetonitrile) was added. The spiro-OMeTAD solution was spin-coated on the top of the active layer at 6000 rpm for 30 s. To complete the fully top cells, 80 nm of ITO layer as a transparent rear-electrode was prepared using a radio frequency magnetron sputtering at 13.56 MHz with a deposition pressure of 2 mTorr. The fabrication of crystalline silicon heterojunction (c-Si-HJ) solar cells was described in the previous report [11].

Characterizations

Transmittance and reflectance properties of PDMS (Sylgard®184) films were measured by an UV-VIS-NIR spectrophotometer (Cary 5000) in the wavelength range of 200-1200 cm^{-1}. The *J-V* characteristics of solar cells were measured using a solar simulator under AM 1.5G light illumination (100 mW/cm^2) (Wacom class AAA simulator). The efficiencies of semitransparent perovskite top cells were measured under an aperture mask of 1 cm^2. The scan rate and voltage step are fixed at 0.02 V/s and 10 mV, respectively. The efficiencies of silicon bottom cells were measured with the same solar simulator with an active area of ~0.96 cm^2. To examine an efficient performance of bottom cells in 4T perovskite/silicon tandem without (called an air-spacer layer) and with PDMS films (called an IML), a semitransparent perovskite-filtered light with the 1 cm^2 aperture mask were stacked on the top of bottom solar cells. Overall efficiencies of 4T perovskite/silicon tandem devices with an air gap and with an IML were calculated.

3. Results and discussion

Anti-reflective polymer film as an intermediate matching layer of silicon solar cell

Due to its anti-reflective polymer, suitable refractive index value, high transparency, hydrophobicity, and straightforward processing method, PDMS was chosen as an IML. To eliminate the air-spacer layer and increase the efficiency, the PDMS films were utilized as an IML in the 4T perovskite/silicon tandem cells. The optical properties of PDMS films coated on glass substrates are illustrated in Figure 1(a-b). Their example image was added to Figure 1(a). From 300 nm to over 1100 nm, the transmittance spectra of uncoated and PDMS-coated bare glasses are presented at 90%. There is no variation in light transmission in the region of long wavelengths. In order to account for the reflectance loss depicted in Figure 1(b), the reflectance spectra of PDMS film coated on glass were 8%, which had a slightly lower than uncoated glass (9–10%). It can observe that the reduction of light reflection has directly produced the improving J_{sc} values of silicon bottom cell. This result indicates that PDMS can be used as an IML in tandem configurations with four terminals in place of an air-spacer layer.

For a preliminary performance to determine the effect of light incidence on the standard silicon solar cells, Figure 1(c) displayed the models consisting of two glasses without and with the PDMS layer, referred to as glass/air gap/glass and glass/PDMS/glass, respectively, stacked on top of single standard silicon solar cells. The *J-V* curve and detail parameters of a standard silicon solar cell, including open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (*FF*) and power conversion efficiency (*PCE*), are depicted in Figure 1(d) and Table 1, respectively. An independent standard silicon solar cell exhibited an initial efficiency of 10.28%, with V_{oc}, J_{sc} and *FF* values of 0.57 V, 27.34 mA/cm^2 and 0.66, respectively. The same silicon solar cell filtered with glass/air gap/glass maintained a J_{sc} of 26.03 mA/cm^2 and a *PCE* of 9.79%. The efficiency and current density of a silicon device filtered with glass, PDMS, or glass were increased to 26.18 mA/cm^2 and 9.82%, respectively. Additionally, the PDMS layer has no noticeable effect on the V_{oc} or *FF*. It has been observed that the use of PDMS in conjunction with silicon bottom cells increases the amount of incident light collected, as well as the current density and efficiency of the silicon bottom cells.

Table 1 Photovoltaic characteristics of standard silicon bottom cell without and with commercial PDMS films

Samples	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF*	*PCE (%)*
Silicon solar cell (unfilter)	0.57	27.34	0.66	10.28
Silicon/glass/air gap/glass	0.57	26.03	0.66	9.79
Silicon/glass/PDMS/glass	0.57	26.18	0.66	9.82

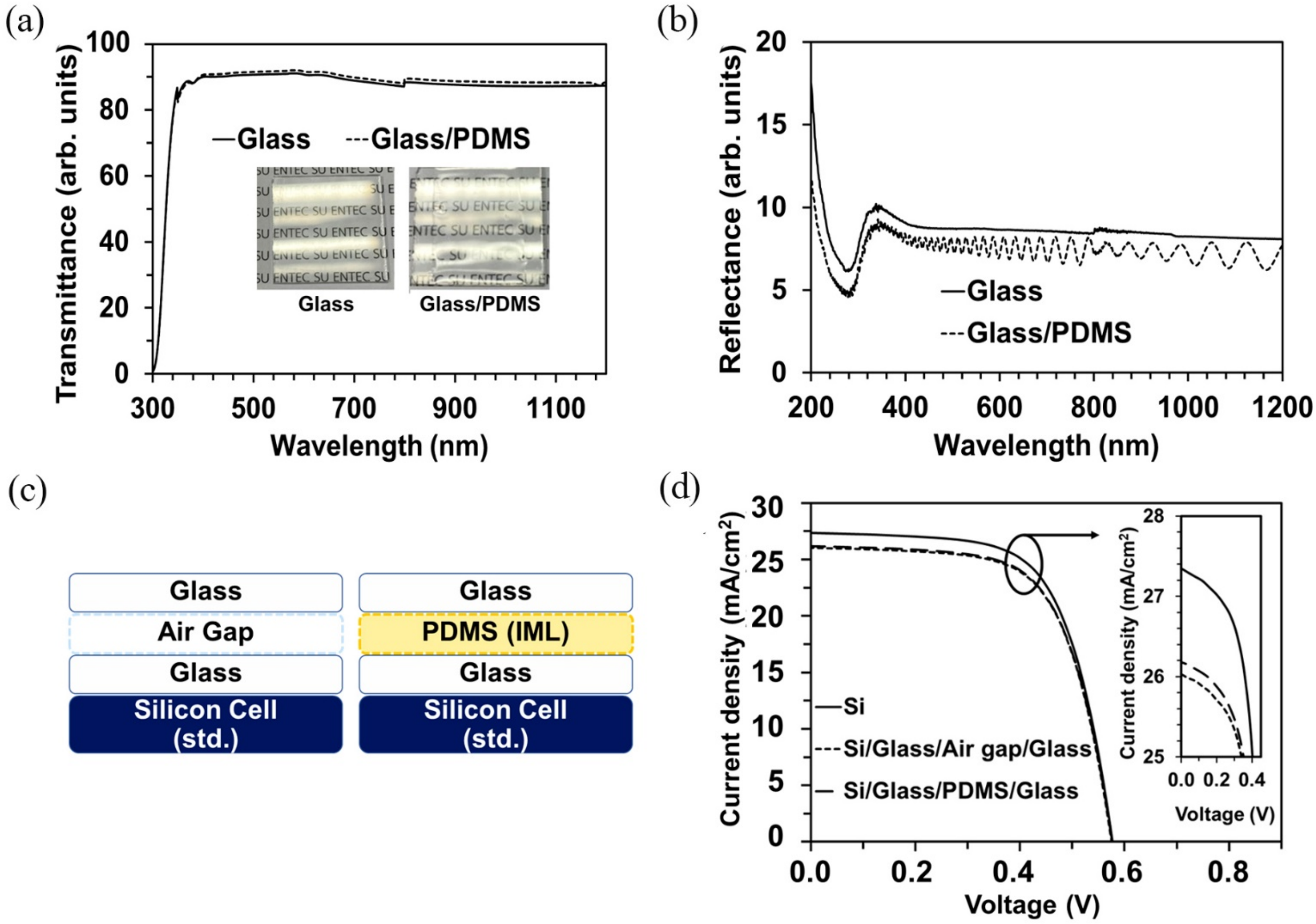

Figure 1 (a) Transmittance, (b) reflectance of glass and PDMS/glass, (c) schematic model, and (d) *J*-*V* characteristic of standard silicon bottom cells with an air gap and PDMS film as an IML. Inset in panel (a) show a photograph of PDMS film coated on glass substrates. Inset in panel (d) is an enlarge scale of the *J*-*V* curve.

Four terminal (4T) perovskite/silicon tandem cell efficiencies

Figure 2(a) depicts the structure of a perovskite/silicon tandem solar cell with four terminals. It has heterojunction silicon bottom cells and semitransparent perovskite top cells, which are separated by an IML and an air gap. Figure 2(b) and Table 2 display the *J*-*V* characteristic spectra and photovoltaic parameters for a 4T perovskite/silicon tandem cell tested with a standard light intensity of 100 mW/cm^2. With a 1 cm^2 aperture mask, the efficiency of independent top and bottom cells (the unfiltered cells) was measured. The semitransparent perovskite cell had the highest *PCE*, at 14.34%, along with the highest V_{oc}, J_{sc} and *FF* values, at 1.11 V, 19.97 mA/cm^2 and 0.65, respectively. While the initial efficiency of the silicon bottom cell was 17.15%, with V_{oc}, J_{sc} and *FF* values of 0.65 V, 33.77 mA/cm^2 and 0.78, respectively, the *PCE* decreased over time. Therefore, the performance of the bottom cell with an air gap and the middle cell with an IML was evaluated using the same silicon solar cell. The filtered silicon cell, which utilized an air gap perovskite cell (no IML), revealed a *PCE* of 6.43% with V_{oc}, J_{sc} and *FF* values of 0.61 V, 13.39 mA/cm^2 and 0.78, respectively. The *PCE* is significantly reduced from 17.15 to 6.43% (representing a reduction of 62.2%). The value of J_{sc} is drastically decreased from 33.77 to 13.39 mA/cm^2 (60.3% reduction) [7,12]. In addition, an air gap layer diminished the amount of light collecting on the bottom cell, resulting in a reduction of current density and efficiency. In this study, a PDMS film with a refractive index of 1.4 was used as an IML to replace the air gap in 4T tandem technologies

[13,14]. Due to its anti-reflective effect, PDMS with hydrophobic and anti-reflective properties could enhance the performance of silicon bottom cells [15]. Compared to the filtered bottom cell with an air gap, the *PCE* and J_{sc} of the bottom cell of the filter with an IML (PDMS film) could be improved by 7.23 % and 14.95 mA/cm^2, respectively. 57.8% of initial silicon performance is attributable to the reduction of *PCE*. Therefore, the overall calculated efficiencies of 4T PSC-silicon tandem devices with an air gap and an IML were calculated to be 20.77% and 21.57%, respectively. Based on the results, a role of the IML reduced the reflectance effects of silicon bottom cell, exhibiting greater light passed through in the cells. Thereby, the J_{sc} and *PCE* of 4T tandem configuration should be enhanced.

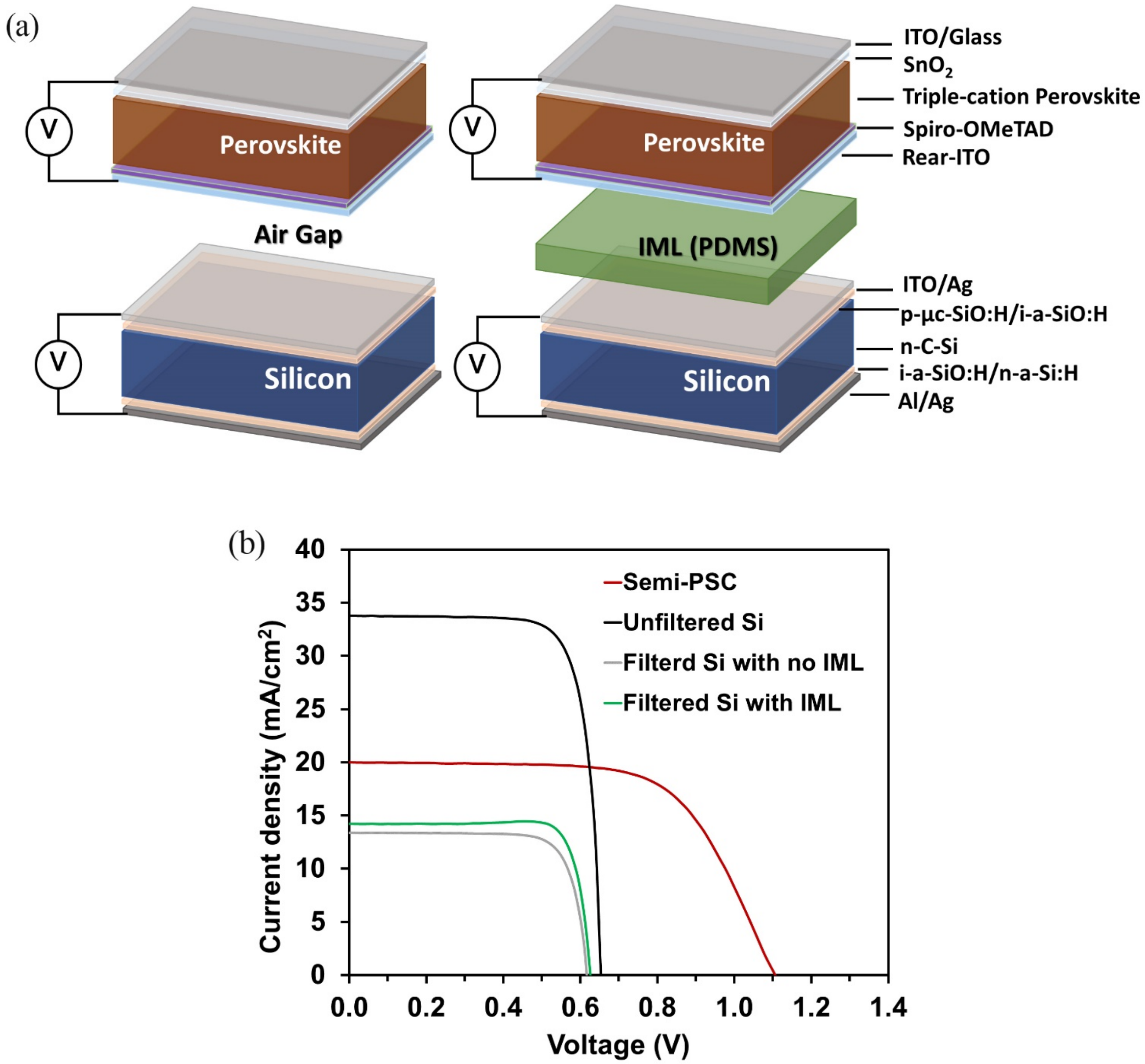

Figure 2 (a) Device architecture of 4 terminal perovskite/silicon tandem solar cells with an air gap and PDMS as an IML and (b) *J-V* curve of semitransparent perovskite top sub cell, unfiltered silicon, and filtered silicon bottom sub cells with and without IML.

Table 2 Photovoltaic parameters of each sub-cells for 4T perovskite/silicon tandem devices

Samples	Active area (cm²)	V_{oc} (V)	J_{sc} (mA/cm²)	FF	PCE (%)
Semitransparent PSC (top cell)	1.00	1.11	19.97	0.65	14.34
Unfiltered silicon solar cell (bottom cell)	0.96	0.65	33.77	0.78	17.15
Filtered silicon solar cell with an air gap	0.96	0.61	13.39	0.78	6.43
Filtered silicon solar cell with an IML	0.96	0.61	14.95	0.79	7.23
Calculated 4T-PSC/silicon tandem					
with an air gap (without an IML)					20.77
with an IML					21.57

4. Conclusion

The 4T perovskite/silicon tandem solar cell comprises individual sub-cells connected by mechanical stacking. An air gap as optical losses can decrease the performance of the four-terminal (4T) tandem structures. In this study, the use of commercial-grade PDMS (Sylgard®184) could serve as an IML because of their excellent properties such as anti-reflective polymer, suitable refractive index value, and high transparency. The PDMS film coated on glass substrate exhibited the light reflectance of 8%, which had a slightly lower than the uncoated glass (9–10%). The reduction of light reflection has directly produced the improving J_{sc} and *PCE* values of silicon bottom cell. With an air gap, the current density of silicon heterojunction devices increases from 13.39 mA/cm^2 to 14.95 mA/cm^2 (with an IML). Consequently, IML between each sub-cells achieved the highest efficiency of 21.57%, while the fully device without an IML exhibited of 20.77%. This method proposed an IML solution to improve the efficiency for further tandem photovoltaic technologies.

Acknowledgment

The authors are sincerely grateful to The Energy Innovation Program, Technology Development Groups (TDGs) project of the National Science and Technology Development Agency (NSTDA), Thailand (grant no P2051358) for providing grant to support this work.

References

[1] P. Tockhorn, J. Sutter, A. Cruz, P. Wagner, K. Jäger, D. Yoo, ..., C. Becker, Nano-optical designs for high-efficiency monolithic perovskite–silicon tandem solar cells, *Nat. Nanotechnol.* **17** (2022) 1214-1221.
[2] National Renewable Energy Laboratory (NREL), PV efficiency chart, From http://www.nrel.gov/pv.
[3] M. De Bastiani, A. S. Subbiah, E. Aydin, F. H. Isikgor, T. G. Allen, S. De Wolf, Recombination junctions for efficient monolithic perovskite-based tandem solar cells: Physical principles, properties, processing and prospects, *Mater. Horiz.* **7** (2020) 2791-2809.
[4] H. Li, W. Zhang, Perovskite tandem solar cells: From fundamentals to commercial deployment, *Chem. Rev.* **120** (2020) 9835-9950.
[5] G. E. Eperon, T. Leijtens, K. A. Bush, R. Prasanna, T. Green, J. T. W. Wang, H. J. Snaith, Perovskite-perovskite tandem photovoltaics with optimized band gaps, *Science* **354** (2016) 861-865.
[6] S. Kim, T. T. Trinh, J. Park, D. P. Pham, S. Lee, H. B. Do, J. Yi, Over 30% efficiency bifacial 4-terminal perovskite-heterojunction silicon tandem solar cells with spectral albedo, *Sci. Rep.* **11** (2021) 15524.
[7] M. Jaysankar, M. Filipič, B. Zielinski, R. Schmager, W. Song, W. Qiu, J. Poortmans, Perovskite–silicon tandem solar modules with optimised light harvesting, *Energy Environ. Sci.* **11** (2018) 1489-1498.

[8] G. Yu, C. Shou, Z. Yang, H. He, Y. Zhang, W. Yang, J. Ye, Optical management of spacer layer of high-performance four-terminal perovskite/silicon tandem solar cells, *Sol. Energy.* **228** (2021) 226-234.

[9] X. Liu, K. Cheng, P. Cui, H. Qi, H. Qin, G. Gu, Z. Du, Hybrid energy harvester with bi-functional nano-wrinkled anti-reflective PDMS film for enhancing energies conversion from sunlight and raindrops, *Nano Energy.* **66** (2019) 104188.

[10] C. A. Charitidis, Nanoscale deformation and nanomechanical properties of polydimethylsiloxane (PDMS), *Ind. Eng. Chem. Res.* **50** (2011) 565-570.

[11] T. Krajangsang, S. Inthisang, J. Sritharathikhun, A. Hongsingthong, A. Limmanee, S. Kittisontirak, K. Sriprapha, An intrinsic amorphous silicon oxide and amorphous silicon stack passivation layer for crystalline silicon heterojunction solar cells, *Thin Solid Films* **628** (2017) 107-111.

[12] L. Xu, J. Liu, F. Toniolo, M. De Bastiani, M. Babics, W. Yan, S. De Wolf, Monolithic perovskite/silicon tandem photovoltaics with minimized cell-to-module losses by refractive-index engineering, *ACS Energy Lett.* **7** (2022) 2370-2372.

[13] A. Hadipour, B. de Boer, P. W. Blom, Solution-processed organic tandem solar cells with embedded optical spacers, *J. Appl. Phys.* **102** (2007) 074506.

[14] G. Yu, C. Shou, Z. Yang, H. He, Y. Zhang, W. Yang, J. Ye, Optical management of spacer layer of high-performance four-terminal perovskite/silicon tandem solar cells, *Sol. Energy* **228** (2021) 226-234.

[15] H. Lee, A. Yi, J. Choi, D. H. Ko, H. J. Kim, Texturing of polydimethylsiloxane surface for anti-reflective films with super-hydrophobicity in solar cell application, *Appl. Surf. Sci.* **584** (2022) 152625.