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## REVIEW

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## 1. Introduction

With the combination of eco-friendly and technological improvements, the global new installed solar photovoltaic (PV) capacity over the past 20 years has grown at a compound annual growth rate (CAGR) of 39.3% (Fig. 1(a)), far outpacing other energy sources (Fig. 1(b)).<sup>1</sup> The strong momentum of the PV industry, as illustrated in Fig. 1(c), comes from its levelized cost of electricity (LCOE) decreasing most rapidly relative to coal,

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A review on monolithic perovskite/c-Si tandem solar cells: progress, challenges, and opportunities

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Two-junction solar cells with higher theoretical power conversion efficiency (PCE) show great potential for application in photovoltaic (PV) systems, among which the perovskite/c-Si tandem solar cell (PSK/c-Si TSC) has been highlighted due to the existing industrial advantages of its bottom-cell. The PSK/c-Si TSC can be classified into four structures (flat, planarized, and conformal structures, and mechanical stacking), while the strengths and weaknesses of these four structures have been lacking deeper investigation and comparison. This review integrates their best experimental spectral response with the simulated optical properties, and concludes that the conformal structure has the highest theoretical PCE (31.4%) and the best optical properties. However, to address the challenges of PCE enhancement of the conformal structure, the authors review the feasibility of textured interface refinement and innovatively propose practical suggestions for electrical optimization. Finally, advances in practical applications of the PSK/c-Si TSC with respect to large-scale manufacturing, stability issues, and bifacial properties are discussed, which will drive the sustainable development of the PV industry and contribute to global carbon neutralization.

wind, and natural gas, *e.g.*, from 358.4 \$  $MW^{-1}$  h<sup>-1</sup> in 2009 to 37.2 \$  $MW^{-1}$  h<sup>-1</sup> in 2019. Among the global PV products, crystalline silicon (c-Si) solar cells have been the leader for 40 years and now have over 95% of the market share (Fig. 1(d)).<sup>1</sup> As cumulative shipments increase, the price of PV modules has also decreased rapidly, from 113.1 \$  $W_p^{-1}$  in 1978 to just 0.20 \$  $W_p^{-1}$  in 2020 (Fig. 1(e)).<sup>1,2</sup> As a result, as shown in Fig. 1(f), the lowest bid price for large-scale PV plants around the world has been reducing over the years, reaching 1.04 cents per kW h in Saudi Arabia (2021).<sup>3</sup> Therefore, the Chinese government has announced that the proportion of PV power generation will rise to 39% by 2050 from the present value of only 3.5% of the total power generation. The US government has even planned to increase the proportion of PV power generation to 40% by 2035.



Chao Gao received his B.S. degree in the School of Physics and Materials Science from Anhui University, China, in 2019. Currently, he is a PhD candidate at the School of Physics and Astronomy, Shanghai Jiao Tong University. His research interests focus on solar energy materials and perovskite/crystalline silicon tandem solar cells.



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The existence of the Shockley-Queisser limit<sup>7</sup> (29.4%) for single-junction c-Si solar cells means that the PV industry must consider a multi-junction tandem scheme for long-term growth and sustainability. Currently, the highest certified power conversion efficiency (PCE) of six-junction III-V solar cells is as high as 47.1% under the concentrated light condition of 143 suns.8 Nevertheless, considering the practical factors such as cost, preparation process, and industry status, the combination of perovskite (PSK) and c-Si is the most recognized by researchers, and their single-junction certified PCE has also reached up to 25.7%9 and 26.7%,9,10 respectively. According to the study,<sup>11</sup> the Si bottom-cell with a 1.12 eV bandgap tandem with the 1.68 eV PSK top-cell can ensure the optimal distribution absorption of solar spectrum irradiation and reduce the heat-loss due to the mismatch of bandgaps. The theoretical limit of PCE of the full-spectrum matched two-junction cell can exceed 43%.12 And in just 6 years, the PSK/c-Si tandem solar cell (TSC) has improved with the PCE soaring from 13.7%<sup>13</sup> initially to 29.8%<sup>9</sup> now, demonstrating the great potential for future industrial applications.14



Dong Ding received his PhD degree in Condensed Matter Physics at the School of Physics and Astronomy from Shanghai Jiao Tong University, China, in 2021. He is currently a postdoctoral researcher at the School of Physics and Astronomy, Shanghai Jiao Tong University. His research interests focus on novel crystalline silicon solar cells, including experiment design and theoretical simulation.

This review summarizes the research progress of three types of solar cells (PSK/c-Si,11,13,15-57 PSK/Cu(In,Ga)Se2 (CIGS),58-61 and PSK/PSK62-80 TSCs) in the 2-terminal (2T) tandem field, and points out their complementary characteristics. We classify the PSK/c-Si TSC reported in the literature so far into flat,<sup>15-25</sup> planarized,44-50,57 and conformal structures11,51-53,56 and mechanical stacking<sup>54</sup> based on their structure types and evaluate the strengths and weaknesses of their preparation schemes (coevaporation + solution, spin-coating, blade-coating, slot-die coating, and physical stacking). From the best experimental spectral response and the simulated optical properties, we conclude that the conformal structure in the PSK/c-Si has the highest theoretical upper limit of PCE compared to its other three counterparts, and remark that the conformal structure is subject to further electrical optimization. We further review the metrics for practical applications of the PSK/c-Si TSC, including large-scale manufacturing, stability issues, and bifacial properties, and conduct a feasibility analysis for commercialization. The present review provides a fresh perspective for the profound experimental exploration and numerical simulation of the PSK/ c-Si TSC, and will contribute to the sustainable development of the PV industry.

# 2. Prospects and advances of the 2T tandem solar cells

At present, the two-junction TSCs are mainly divided into three categories: PSK/c-Si, PSK/CIGS, and PSK/PSK. Their highest certified PCEs are 29.8%,<sup>9</sup> 24.2%,<sup>9</sup> and 26.4%,<sup>80</sup> respectively. Fig. 2(a) illustrates the maximum PCE evolution of the 2T TSCs taken from the literature or authoritative reports, where we can observe that the development of the PSK/c-Si TSC is steadily moving forward compared to the others, and its PCE is increasing the most dramatically.

The PSK/c-Si TSC has a richer structure than the PSK/PSK and PSK/CIGS TSCs owing to the pyramidal interface of the Si bottom-cell (the other two solar cells are planar), including flat (Fig. 2(b1)), planarized (Fig. 2(b2)), and conformal structures (Fig. 2(b3)), and mechanical stacking (Fig. 2(b4)). For PSK/PSK



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**Fig. 1** Evolution and status of solar PVs.<sup>1–6</sup> (a) Annual amount of new PV installed capacity over the past 20 years. (b) CAGR of various energy sources. GBE, geothermal and biomass energy. (c) Changes in LCOE of various energy sources over 10 years. (d) Share of c-Si solar cell products in the global PV annual products. (e) Relationship between average module prices and cumulative PV module shipments from 1976 to 2020. (f) Recent yearly lowest bid prices for large-scale PV plants in the world. UAE, United Arab Emirates.

solar cells, the preparation process is severely restricted by the flatness of the substrate due to the non-stoichiometric ratio synthesis of the bottom-cell (solution-based methodology), so the structure is only flat. To facilitate the scientific investigation of PSK/PSK TSCs, we summarize the constraints as follows: (1) optical losses caused by the limited light trapping ability of the flat structure and the shading effect of Ag<sup>79</sup>/Cu<sup>69</sup>/Au<sup>70,76</sup> metal



**Fig. 2** (a) Maximum PCE evolution of the 2T TSCs (taken from literature or authoritative reports).<sup>11,13,15–79</sup> Their structure schematics including (b1) flat, (b2) planarized, and (b3) conformal structures, and (b4) mechanical stacking.

clusters in the tunnel recombination junction; (2) additional compact intermediate layers (ALD-SnO2,<sup>70,76</sup> ITO,<sup>68,73</sup> AZO,<sup>72</sup> etc.) or co-evaporation<sup>62,65</sup> is required to prevent dissolution of the bottom-cell during the preparation of narrow-bandgap PSK; and (3) narrow-bandgap PSK preparation requires partial substitution of Sn for Pb,<sup>63,64,68,70,72,73,75-79</sup> but Sn<sup>2+</sup> is highly susceptible to oxidation to Sn<sup>4+</sup>, resulting in poor stability. The latest literature reports indicate that the highest PCE of Pb/Sn hybrid singlejunction PSK solar cells is only 23.3%,81 which reveals the challenges and opportunities. There are two structures for the PSK/CIGS TSC: flat and mechanical stacking. The scientific research issues for the CIGS bottom-cell are: (1) the CIGS solar cell has a weak light trapping capability due to the lack of wavelength-matching arrayed morphological undulations;59,60 (2) the regulation of the Ga component in CIGS is more sophisticated in order to achieve an appropriate bandgap; (3) the best research-cell PCE of CIGS solar cells (23.4%<sup>9</sup>) is lower than that of Si solar cells (26.7%<sup>9</sup>), and there is a huge discrepancy between their champion module PCEs (CIGS 19.2%<sup>82</sup> vs. Si 24.4%<sup>82</sup>); and (4) the CIGS manufacturing process involves a wide variety of elements, while the raw materials required for Si solar cells are plentiful in the Earth. If the topics discussed above are solved, it will greatly facilitate the experiments and future industrialization of PSK/PSK and PSK/CIGS TSCs.

Table 1 summarizes the reported 2T PSK/c-Si TSCs from 2015 to 2021. The PSK/c-Si TSCs can be further categorized into two groups according to the variation of the bottom-cell type: Si

Table 1 Overview of 2T PSK/c-Si TSCs reported from 2015 to 2021, and classified according to their structures<sup>a</sup>

Structure	Top cell		_						
	Architecture	$E_{\rm g}$ (eV)	Bottom cell	V <sub>OC</sub> (V)	$J_{ m SC} ({ m mA} \ { m cm}^{-2})$	FF (%)	PCE (%)	Active area (cm <sup>2</sup> )	Ref.
Flat	LiF/IZO/SnO <sub>2</sub> /C <sub>60</sub> (LiF)/Cs <sub>0.05</sub> (FA <sub>0.77</sub> MA <sub>0.23</sub> ) <sub>0.95</sub> Pb(I <sub>0.77</sub> Br <sub>0.23</sub> ) <sub>3</sub> / SAM(PTAA)/ITO	1.68	SHJ	1.90	19.26	79.5	29.15	1.06	15
	LiF/ITO/MoO <sub>3</sub> /spiro-OMeTAD/(FA,MA)Pb(I,Br) <sub>3</sub> /SnO <sub>2</sub> /ITO MgF <sub>2</sub> /ITO/spiro-OMeTAD/FA <sub>0.75</sub> Cs <sub>0.25</sub> Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /PCBM:PMMA/	 1.70	ЅНЈ ЅНЈ	1.78 1.84	14 15.2	79.5 77.3	19.9 21.6	0.16 0.25	16 17
	PDMS/ITO/SnO <sub>2</sub> /C <sub>60</sub> /FA <sub>0.75</sub> Cs <sub>0.25</sub> Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /PTAA/ITO LiF/ITO/SnO <sub>2</sub> (ZTO)/PC <sub>60</sub> BM/LiF/Cs <sub>0.17</sub> FA <sub>0.83</sub> Pb(Br <sub>0.17</sub> I <sub>0.83</sub> ) <sub>3</sub> /NiO/	1.68 1.63	SHJ SHJ	1.77 1.65	18.4 18.1	77 79	25 23.6	1 1	18 19
	ITO MgF <sub>2</sub> /IZO/SnO <sub>2</sub> /C <sub>60</sub> /ICBA/Cs <sub>0.15</sub> (FA <sub>0.83</sub> MA <sub>0.17</sub> ) <sub>0.85</sub> Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> / PTAA/ITO	1.64	SHJ	1.80	17.8	79.4	25.4	_	20
	PDMS/ITO/MOO <sub>x</sub> /spiro-OMeTAD/	1.67	SHJ	1.75	16.89	74.2	21.93	0.13	21
	CS <sub>0.08</sub> FA <sub>0.69</sub> MA <sub>0.23</sub> PD(I <sub>0.69</sub> Br <sub>0.23</sub> ) <sub>3</sub> /SnO <sub>2</sub> /11O ITO/MoO <sub>x</sub> /spiro-OMeTAD/CS <sub>0.08</sub> FA <sub>0.69</sub> MA <sub>0.23</sub> Pb(I <sub>0.69</sub> Br <sub>0.23</sub> ) <sub>3</sub> /SnO <sub>2</sub> / ITO	1.67	SHJ	1.83	16.74	70	21.31	0.13	22
	LM-foil/IZO/SnO <sub>2</sub> /C <sub>60</sub> /Cs <sub>0.05</sub> (MA <sub>0.17</sub> FA <sub>0.83</sub> )Pb <sub>1.1</sub> (I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub> /PTAA/	1.63	SHJ	1.76	18.5	78.5	25.5	0.81	23
	LiF/IZO/ZnO/PCBM/(FAPbI <sub>3</sub> ) <sub>0.8</sub> (MAPbBr <sub>3</sub> ) <sub>0.2</sub> /PTAA/ITO	1.64	SHO	1.65	16.12	79.9	21.19	0.135	24
	ITO/C <sub>60</sub> /PEIE/(FA <sub>0.65</sub> MA <sub>0.2</sub> Cs <sub>0.15</sub> )Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /PTAA/ITO	1.68	SHJ	1.76	19.2	79.2	26.7	0.188	25
	LiF/IZO/SnO <sub>2</sub> /C <sub>60</sub> /Cs <sub>0.05</sub> (MA <sub>0.83</sub> FA <sub>0.17</sub> )Pb(I <sub>0.83</sub> Br <sub>0.17</sub> ) <sub>3</sub> /PTAA/ITO	1.63	SHJ	1.77	19.22	76.6	26.06	0.771	26
	LiF/N-Ag/spiro-OMeTAD/MAPbI <sub>3</sub> /TiO <sub>2</sub>	1.61	SHO	1.58	11.5	75	13.7	1	13
	LiF/ITO/BCP/PC <sub>61</sub> PM/Cs <sub>0.05</sub> (FA <sub>0.83</sub> MA <sub>0.17</sub> ) <sub>0.95</sub> Pb(I <sub>0.82</sub> Br <sub>0.18</sub> ) <sub>3</sub> /NPD/ polyTPD/ITO	1.63	SHJ	1.79	19.02	74.6	25.43	1.088	27
	ITO/MoO <sub>x</sub> /spiro-OMeTAD/FA <sub>0.5</sub> MA <sub>0.38</sub> Cs <sub>0.12</sub> PbI <sub>2.04</sub> Br <sub>0.96</sub> /SnO <sub>2</sub> / ITO	1.69	SHJ	1.66	16.5	81.1	22.22	0.06	28
	ITO/MoO <sub>x</sub> /spiro-OMeTAD/MA <sub>0.37</sub> FA <sub>0.48</sub> Cs <sub>0.15</sub> PbI <sub>2.01</sub> Br <sub>0.99</sub> /SnO <sub>2</sub> / ITO	1.69	SHJ	1.70	15.25	79.2	20.57	0.03	29
	MgF <sub>2</sub> /IZO/MoO <sub>x</sub> /spiro-OMeTAD/Cs <sub>0.19</sub> MA <sub>0.81</sub> PbI <sub>3</sub> /C <sub>60</sub>	1.59	SHJ	1.75	16.8	77.1	22.7	0.25	30
	MgF <sub>2</sub> /ITO/SnO <sub>x</sub> /C <sub>60</sub> /FA <sub>0.75</sub> Cs <sub>0.25</sub> Pb(I <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /PFN/PTAA/ITO	1.68	SHJ	1.77	17.7	80.3	25.1	0.25	31
	ARF/IZO/MoO <sub>x</sub> /spiro-OMeTAD(PTAA)/ Cs <sub>0.05</sub> Rb <sub>0.05</sub> FA <sub>0.765</sub> MA <sub>0.135</sub> PbI <sub>2.55</sub> Br <sub>0.45</sub> /TiO <sub>2</sub>	1.63	SHO	1.76	17.8	78.1	24.5	1	32
	ITO/IO:H/MoO <sub>x</sub> /spiro-OMeTAD/MAPbI <sub>3</sub> /TiO <sub>2</sub> /ZTO	1.60	SHO	1.64	15.3	64.8	16.3	1.43	33
	ITO/IO:H/MOO <sub>x</sub> /spiro-OMeTAD/MAPbI <sub>3</sub> /PCBM(PEIE)/IZO ARF/IZO/MoO <sub>x</sub> /spiro-OMeTAD/	1.60 1.62	SHJ SHO	1.69 1.75	15.8 17.6	79.9 73.8	21.4 22.8	0.17 1	34 35
	Cs <sub>0.07</sub> Rb <sub>0.03</sub> FA <sub>0.765</sub> MA <sub>0.135</sub> PbI <sub>2.55</sub> Br <sub>0.45</sub> /TiO <sub>x</sub> /ITO PDMS/ITO/SnO/C <sub>60</sub> /LiF/FA <sub>0.75</sub> Cs <sub>0.25</sub> Pb( <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /PFN/polyTPD/ NiO_/ITO	1.67	SHJ	1.89	19.12	75.3	27.13	1	36
	$ARF/ITO/MoO_s/spiro-OMeTAD/MAPhI_s/SpO_s$	1 58	SHO	1 68	16.1	78	21	4	37
	ARE/ITO/MOO <sub>2</sub> /spiro-OMeTAD/FAMAPhI <sub>2</sub> Br /SnO <sub>2</sub>	1.60	SHO	1.00	16.5	81	23.1	4	38
	$ARF/ITO/MOO_3/spiro-OMeTAD/(FAPbI_2)_{0.22}(MAPbBr_2)_{0.17}/SnO_2$	1.59	SHO	1.74	16.2	78	21.8	16	39
	ITO/MOQ./spiro-OMeTAD/(Cs.FA.MA)Pb(I.Br) <sub>2</sub> /SnO <sub>2</sub> /ITO/TRL	1.65	SHI	1.78	17.82	75	23.73	0.13	40
	ITO/MoO <sub>x</sub> /spiro-OMeTAD/(FAPbI <sub>3</sub> ) <sub>0.75</sub> (MAPbBr <sub>3</sub> ) <sub>0.25</sub> /SnO <sub>2</sub> /ITO	_	SHI	1.71	15.49	71	18.81	0.13	41
	$MgF_2/ITO/SnO_2/C_{60}/Cs_{0.17}FA_{0.83}PbI_{0.83}Br_{0.17}/NiO/ITO$	1.63	SHJ	1.72	17.48	75	22.6	57.4	42
	ARF/ITO/MoO <sub>x</sub> /spiro-OMeTAD/Cs <sub>0.05</sub> MA <sub>0.15</sub> FA <sub>0.8</sub> PbI <sub>2.25</sub> Br <sub>0.75</sub> / SnO <sub>2</sub> /ITO	1.67	SHJ	1.93	16.92	74	24.16	0.86	43
	MgF <sub>2</sub> /FS/ITO/PTAA/CuSCN/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PC <sub>60</sub> BM/ZnO:Al/PEI/ TCA/N-Ag/ITO	1.61	SHJ	1.78	14.7	80.4	21	0.104	55
Planarized	$\label{eq:mgf2} \begin{split} MgF_2/IZO/TPBI/VO_x/spiro-TTB/Cs_{0.05}MA_{0.15}FA_{0.8}Pb(I_{0.75}Br_{0.25})_3/\\ C_{60}-NbO_x/ITO \end{split}$	1.68	SHJ	1.83	19.5	75.9	27.1	0.1	44
	PDMS/ITO/SnO <sub>2</sub> /C <sub>60</sub> /Cs <sub>0.1</sub> MA <sub>0.9</sub> Pb(I <sub>0.9</sub> Br <sub>0.1</sub> ) <sub>3</sub> /PTAA/ITO	—	SHJ	1.82	19.2	75.3	26.2	_	45
	MgF <sub>2</sub> /IZO/SnO <sub>2</sub> /C <sub>60</sub> /(Cs,FA,MA)Pb(I,Br) <sub>3</sub> /NiO <sub>x</sub>	1.68	SHJ	1.80	18.46	75.9	25.21	0.832	46
	MgF <sub>2</sub> /IZO/LiF/C <sub>60</sub> /SnO <sub>x</sub> /Cs <sub>0.05</sub> MA <sub>0.15</sub> FA <sub>0.8</sub> PbI <sub>2.25</sub> Br <sub>0.75</sub> /NiO <sub>x</sub> /InO <sub>x</sub>	1.68	SHJ	1.78	19.08	75.3	25.71	0.832	47
	$MgF_2/IZO/SnO_2/C_{60}/Cs_{0.15}MA_{0.15}FA_{0.7}Pb(I_{0.8}Br_{0.2})_3/SAM/ITO$	1.68	SHJ	1.84	19.6	76	27.4	1.03	48
	MgF <sub>2</sub> /IZO/SnO <sub>2</sub> /C <sub>60</sub> /MAPb(l <sub>0.75</sub> Br <sub>0.25</sub> ) <sub>3</sub> /PTAA/NiO <sub>x</sub> /ITO MgF <sub>2</sub> /IZO/SnO <sub>x</sub> /C <sub>60</sub> /LiF/Cs <sub>0.15</sub> MA <sub>0.15</sub> FA <sub>0.7</sub> Pb(l <sub>0.8</sub> Br <sub>0.2</sub> ) <sub>3</sub> /N719/	1.68 $1.68$	SHJ SHJ	1.76 1.78	19.2 19.2	70 76.8	23.8 26.2	1 1.03	49 50
	$\label{eq:linear} \begin{split} &NiO_x/ITO \\ &MgF_2/IZO/SnO_2/C_{60}/LiF/Cs_{0.05}FA_{0.8}MA_{0.15}Pb(I_{0.75}Br_{0.25})_3/2PACz/ \\ & \end{split}$	1.68	SHJ	1.86	19.6	78.2	28.6	1.03	57
		1.52	0117	4 7 4	10.0	70.4	05.4	0.022	11
Conformal	$\operatorname{MgF}_{2}/\operatorname{IZO}(\operatorname{SnO}_{2}/\operatorname{C}_{6}/(\operatorname{CS},\operatorname{FA})\operatorname{Pb}(1,\operatorname{Br})_{3}/\operatorname{Spiro-TTB}$	1.63	SHJ	1.74	19.8	/3.1	25.1	0.832	11
structure	$\operatorname{Mgr}_2/\operatorname{IZO}/\operatorname{SnO}_2/\operatorname{C}_{60}/\operatorname{LIF}/(\operatorname{CS},\operatorname{FA})\operatorname{Pb}(\operatorname{I},\operatorname{Br})_3/\operatorname{Spiro-TTB}$	1.63	SHO	1.74	19.5	/4.7	25.1	1.42	51
	12U/SNU <sub>2</sub> /U <sub>60</sub> /MA <sub>0.5</sub> FA <sub>0.63</sub> PDI <sub>3.13</sub> /MeO-2PACz/ITO	1.53	ѕнј	1.69	18.5/	/8.8	24.6	1.008	52

#### Table 1 (Contd.)

Structure	Top cell								
	Architecture	Eg (eV)	Bottom cell	V <sub>OC</sub> (V)	$J_{ m SC} \left( { m mA} \atop { m cm}^{-2}  ight)$	FF (%)	PCE (%)	Active area (cm²)	Ref.
	MgF <sub>2</sub> /IZO/SnO <sub>2</sub> /C <sub>60</sub> /LiF/Cs <sub>x</sub> FA <sub>1-x</sub> Pb(I,Br) <sub>3</sub> /spiro-TTB/ITO	1.60	SHJ	1.79	19.5	73.1	25.2	1.42	53
	MgF <sub>2</sub> /IZO/SnO <sub>2</sub> /C <sub>60</sub> /LiF/FA <sub>0.9</sub> Cs <sub>0.1</sub> PbI <sub>2.87</sub> Br <sub>0.13</sub> /CsBr/spiro-TTB	_	SHJ	1.81	19.78	76.9	27.48	0.509	56
Mechanical stacking	$Glass/FTO/TiO_{2}/(Cs_{0.06}FA_{0.78}MA_{0.16})Pb(Br_{0.17}I_{0.83})_{3}/spiro-OMeTAD(PTAA)/ITO$	1.64	SHJ	1.80	18.81	77.5	26.3	1.43	54

<sup>a</sup> N-Ag: Ag nanowires; ARF: anti-reflection film; FS: fused silica; TCA: transparent conductive adhesive.

homojunction (SHO)<sup>13,24,32,33,35,37-39,51</sup> and Si heterojunction (SHI),<sup>11,15-23,25-31,34,36,40-42,44-50,52-54</sup> with the highest PCEs of 25.1%<sup>51</sup> and 29.15%<sup>15</sup> reported, respectively. Since the dielectric layer  $(SiO_x, SiN_x, AlO_x, etc.^{32,33,35,37-39,51})$  with passivation function is located in the outermost layer of the homojunction solar cell, there are two options: one is to discard the dielectric layer, and the middle layers are the entire surface contact;<sup>13,24,33,51</sup> the other is to groove it and make it electrically conductive by local contact.32,35,37-39 This makes avoiding optical parasitic absorption and reducing electrical recombination incompatible, so the PCE is universally low. To maximize passivation and optical absorption, Nogay et al.51 modified the p-type tunnel oxide passivated contact (TOPCon) structure to fabricate a bottom-cell with a pyramid-textured surface (optical) and two tunneling layers (electrical), resulting in a tandem PCE of 25.1%. However, with ultrathin SiO<sub>2</sub>, nanocrystalline SiC<sub>x</sub>, and poly-Si it is difficult to obtain uniformity and repeatability in the pyramidtextured interface, so they can only remain in the laboratory and are not guaranteed in the PV industry. The TOPCon manufacturing line uses a single-sided tunnel junction fabricated on a flat surface. The industrial PCE of SHJ solar cells has already reached up to 26.3% (area 274.3 cm<sup>2</sup>),<sup>83</sup> and their robust passivation of intrinsic amorphous Si layers, symmetrical textures and inherent transparent conductive oxide (TCO) make them ideal collaborators for application in the PSK/c-Si TSC. Although the SHJ has obvious technical advantages, the SHO has more industrial strengths, and the two are generally comparable.

PSK is one of the hottest materials currently being investigated and its strengths for photovoltaic applications are (1) high defect tolerance:<sup>84,85</sup> it does not require a high degree of purity and has low demand on the fabrication process; (2) bandgap tunability:<sup>86–88</sup> suitable PSK cells can be prepared based on the different bandgap of the bottom-cell to maximize the utilization of the solar spectrum; (3) high absorption coefficient:<sup>89</sup> adequate light absorption can be achieved with PSK thicknesses in the nano-scale, and material usage and costs are greatly reduced; and (4) steep absorption edge:<sup>90–92</sup> this property reveals that the PSK material has a very obvious absorption cutoff, so it does not affect the work of the bottom-cell at certain wavelengths. In summary, PSK is an ideal material for building TSCs, and PSK-based TSCs have unlimited potential for further development. Overall, the three TSCs are only options in the field of research, and there is no superiority or inferiority. Although PSK/c-Si has the advantages of the c-Si bottom-cell and higher tandem PCE, PSK/PSK and PSK/CIGS can utilize the advantages of thin film solar cells to develop flexible devices and make up for the shortage of Si.<sup>72</sup> Currently, all three TSCs are developing very rapidly and industrialization may be imminent. Due to the complementary nature of their features, other tandem technologies could provide viable solutions for PCE breakthroughs in PSK/c-Si TSCs.

## 3. PSK preparation approach for the PSK/c-Si TSC

The preparation of PSK for the PSK/c-Si TSC is different from the preparation of single-junction PSK, which can result in restricted synthesis methods and the failure of some attempts due to the Si substrate roughness.<sup>93,94</sup> Moreover, some PSK preparation methods (one-step co-evaporation, spray-coating, inkjet printing, *etc.*) cannot be simply applied to PSK/c-Si TSCs. Currently, the main preparation methods are shown in Fig. 3(a–e).

For the flat structure, there are two preparation schemes reported in the literature: evaporation + solution (Fig. 3(a))<sup>34</sup> and spin-coating (Fig. 3(b)).<sup>13,15-33</sup> For the first scenario, Werner et al.34 employed a strategy of thermal evaporation to deposit lead(II) iodide (PbI<sub>2</sub>) followed by the solution-process with methylammonium iodide (MAI), achieving a PCE of 19.2% over an area of 1.22 cm<sup>2</sup> on the SHJ bottom-cell. For the second scenario, due to the lower threshold and the many advantages of manufacturing, spin-coating gradually becomes a typical and common methodology for the synthesis of the top-cell. In 2015, Mailoa et al.13 used a two-step spin-coating on the SHO bottomcell to attain the first PSK/c-Si TSC with an initial PCE of 13.7%. As the study progressed, Al-Ashouri et al.<sup>15</sup> achieved a PCE of 29.15% in 2020 on an SHJ by enhancing hole extraction. Currently, spin-coating is one of the commonly used preparation schemes for single-junction PSK solar cells with a mature process and high PCEs of the produced solar cells. For TSCs with a flat structure, the roughness of the Si substrate is consistent with that of conductive glass. The preparation process of single-junction PSK can be fully followed, so this is



**Fig. 3** Preparation methods of 2T PSK/c-Si TSC. (a) Co-evaporation + solution. (b) Spin-coating. (c) Blade-coating. Reproduced with permission,<sup>45</sup> copyright 2020, Elsevier. (d) Slot-die coating. Reproduced with permission,<sup>49</sup> copyright 2020, American Chemical Society. (e) Physical stacking. Reproduced with permission,<sup>54</sup> copyright 2020, Elsevier.

the reason why the flat structure has been studied the most. The drawbacks of the flat structure are: firstly, the polished surface is not compatible with the Si PV industry; secondly, the reflection loss of the flat structure is serious, which reduces the shortcircuit current density.

To reduce the reflection loss, a significant amount of research has focused on the textured architecture, with planarized structure being one attempt. Planarized structure has been achieved in the literature by spin-coating (Fig. 3(b)),<sup>44,46-48,50,57</sup> blade-coating (Fig. 3(c)),<sup>45</sup> and slot-die coating (Fig. 3(d)).<sup>49</sup> Liu et al.<sup>57</sup> utilized the spin-coating on an SHJ to prepare high-quality wide-bandgap PSK by addition of carbazole molecules (suppressing the secondary phase), achieving a PCE of 28.6%. Chen et al.45 employed a N2-assisted blade-coating process on an SHJ to obtain a tandem PCE of 26.2% by rapid blow-drying of crystalline PSK. Meanwhile, Subbiah et al.49 used slot-die coating on an SHJ to fabricate a 1.68 eV bandgap PSK and ultimately achieved a PCE of 23.8% on 1  $\text{cm}^2$  in 2020. The demerit of this structure is that the PSK layer is too thick, making carrier extraction and transport complicated, and there is still a lack of light trapping on its forward plane.

Another way of achieving a tandem configuration on the textured surface is facile physical stacking (Fig. 3(e)). Lamanna *et al.*<sup>54</sup> combined a PSK solar cell with an SHJ solar cell through an intermediate Ag finger to obtain a 26.3% PCE on an area of 1.43 cm<sup>2</sup>. Compared with the face-contact tandem, physical stacking has only Ag interconnections, so the metal grids and busbars in the middle layer of the TSC will cause optical

shading, and the extra PV components will also increase the cost.

In addition to what has been discussed above, Sahli et al.53 reported in 2018 the conformal structure with unique optical properties with a PCE of 25.2%. The single synthesis process is shown in Fig. 3(a). To ensure the conformal texture of the PSK layer, the inorganic halides (PbI<sub>2</sub> and CsBr) must be thermally co-evaporated to form a mesoporous template in the first step, and the organic halides (FAI and FABr) need to be spin-coated and finally converted to PSK in the second step. This means that the preparation of high-quality conformal PSK is bound to face many difficulties: (1) how to maintain the elemental ratio during the evaporation process; (2) the control of the nucleation to film formation procedure (two-step method); and (3) how to obtain the PSK with a suitable bandgap in the multi-component tuning. Although the progress of the conformal structure has been very slow on account of the great challenges in fabrication methods, together with the laboratory PCE being lower than that of flat structure, it is still favored by many groups.<sup>11,51-53</sup> We will explore in depth in Section 4 what exactly are the advantages of the conformal structure.

In conclusion, due to the different crystallization dynamics of each structure system (flat, planarized, and conformal structures, and mechanical stacking), these five preparation schemes have their own strengths and weaknesses. For coevaporation + solution,<sup>11,34,51-53,95</sup> the scheme can be divided into two steps. The inorganic halides synthesized by the first step of thermal co-evaporation have the advantages of robust adhesion, uniform conformability, and excellent



**Fig. 4** Spectral response of the PSK/c-Si TSC with four structures (taken from the optimal values in the relevant literature). Adjustments were made to coloring and text for formatting consistency. (a) Flat. Reproduced with permission,<sup>15</sup> copyright 2020, The American Association for the Advancement of Science. (b) Planarized. Reproduced with permission,<sup>57</sup> copyright 2021, Elsevier. (c) Conformal structure. Reproduced with permission,<sup>53</sup> copyright 2018, Springer Nature. (d) Mechanical stacking. Reproduced with permission,<sup>54</sup> copyright 2020, Elsevier. Numerical analysis of ideal models: (e) PCE, (f)  $J_{SC}$ , (g) FF, and (h)  $V_{OC}$ , together with the experimental data (best EQE in the literature) for comparison.

crystallization, 52,56 but the advantages of large-scale preparation may be restricted since the second step involves the solution process. The spin-coating<sup>15-23,96</sup> technique has unparalleled characteristics in terms of installation investment cost and high PCE, but it is far inferior to blade-coating45 and slot-die coating49 in terms of large-scale manufacturing issues. Although printing methods with low material usage can be performed in an ambient atmosphere, the shortcomings lie in the contact between the substrate and the blade, where improper PSK crystallization may cause blade contamination and poor repeatability. Unlike the direct nucleation and film formation of PSK on Si substrates, physical stacking<sup>54</sup> has the simplest and easiest operation, but the two independently fabricated devices require special connection fixtures when working or testing, which is similar to the 4-terminal (4T) configuration97 if the metal bonding of the intermediate layer is removed. Therefore, it is essential to choose the corresponding preparation technique according to the specificity of the device configuration during the experiment or production line.

# 4. Advantages and potential of the conformal structure

### 4.1. Superior spectral response

Fig. 4(a–d) present the best external quantum efficiency (EQE) spectra of the PSK/c-Si TSC for the four structures (flat,<sup>15</sup> planarized,<sup>57</sup> and conformal structures,<sup>53</sup> and mechanical stack-ing<sup>54</sup>) in the literature. The benefits of the conformal structure are as follows. On the one hand, we can find the smallest reflectance (*R*) curve in the conformal structure case, indicating that the addition of texture helps light trapping. Since the c-Si bottom-cell has a thickness of about 250  $\mu$ m essentially

without transmission, it is always theoretically possible to achieve current matching by adjusting the thickness of the PSK layer,<sup>98,99</sup> which implies that except for carrier electrical losses, the larger the 1 - R the higher the current density it obtains. On the other hand, EQE represents the efficiency of converting photons to electron-hole pairs at different wavelengths, and the corresponding current density can be calculated by integration. Since the short-circuit current density of the TSC will be limited by the minimum current density of the two sub-cells, it can be observed from Fig. 4(a–d) that the current densities of the flat, planarized, and conformal structures and mechanical stacking are 19.41, 19.74, 20.1, and 18.4 mA cm<sup>-2</sup>, respectively, with the largest value for the conformal structure, indicating its robust spectral response.

To further investigate the substantial impact of the spectral response, we treated c-Si and PSK solar cells as ideal Shockley diodes and performed numerical calculations, a methodology that has been adopted in numerous literature studies,98-101 and the outcomes are shown in Fig. 4(e–h). We take 20.1 mA cm $^{-2}$  as short-circuit current to calculate the theoretical  $V_{OC} = 1.9$  V, FF = 82.34%, and PCE = 31.4% for the conformal structure; however, the PCEs of the flat and planarized structures and mechanical stacking are 30.6%, 31.0%, and 28.5%, respectively, demonstrating that the conformal structure has the highest PCE. Therefore, we can conclude that the conformal structure will be prominent in the PSK/c-Si TSC, since the nano-scale PSK layer is favorable for both strong light trapping and low parasitic absorption. It is worth noting that the PSK of the conformal structure under this model is still 0.08 eV away from the optimal bandgap (1.68 eV),11 which means that the PCE of the conformal structure has much room for improvement. Nevertheless, contrary to the numerical results, the J-V test PCE (Fig. 4(e)) of



Fig. 5 Optical performance obtained from numerical simulation of the 2T PSK/c-Si TSC. (a) Schematic diagrams of the six structures, and their respective ideal  $J_{SC}$ . AR, anti-reflection. Reproduced with permission,<sup>106</sup> copyright 2016, Optical Society of America. (b1)  $E_z$ -field outputs of flat and (b2) conformal structures at  $\lambda = 785$  nm. Reproduced with permission,<sup>107</sup> copyright 2021, American Chemical Society. (c) PCE in relation to the conformality (angle difference) and thickness of the PSK layer. The pyramid angle difference is between the inclination of the PSK and the inclination of the c-Si pyramid. Reproduced with permission,<sup>99</sup> copyright 2020, John Wiley and Sons. Theoretical quantum efficiency of (d1) the PSK top-cell and (d2) c-Si bottom-cell, with the pyramid-scale from flat to 1.5  $\mu$ m and a fixed period-to-height ratio. Period is the horizontal width of the pyramid and is interpreted as flat when the period is zero. Reproduced with permission,<sup>105</sup> copyright 2020, American Chemical Society. (e) Reflected current density losses ( $J_{SC}^{(R)}$ ) due to different periods of top ( $P_{top}$ ) and bottom ( $P_{bottom}$ ) c-Si textures. Reproduced with permission,<sup>98</sup> copyright 2018, John Wiley and Sons.

permission,<sup>98</sup> copyright 2018, John Wiley and Sons. the conformal structure is only 25.2%,<sup>53</sup> which is obviously lower than those of the other three structures (flat 29.15%,<sup>15</sup> planarized 28.6%,<sup>57</sup> and mechanical stacking 26.3%<sup>54</sup>). The reason is that the ideal Shockley diode model is no longer valid due to the presence of pyramid-textures, and there must be large variations in their electrical properties, as we will illustrate

### 4.2. Authoritative optical simulation

in Section 4.3.

Numerous publications<sup>98,99,102–108</sup> on the structural optimization aspects of the PSK/c-Si TSC have been reported in computational simulations, and the light management design with significant implications will certainly provide substantial guidance for experiments as well.<sup>109</sup> As shown in Fig. 5(a), Santbergen *et al.*<sup>106</sup> have found that pyramid-textures can

dramatically increase the current density of the PSK/c-Si TSC from 17.28 to 20.25 mA  $\rm cm^{-2}$  and the structural evolution diagram can illustrate that roughness has a huge optical dominance. A mutually supporting result has been reported by Tennyson *et al.*,<sup>107</sup> that the addition of texture enhances the  $E_{\tau}$ field in-coupling and its out-coupling also becomes inhomogeneous, attributed to the increased photon capture within the prismatic valley by comparing Fig. 5(b1) with 5(b2). Obviously, the improvement in optical performance is well illustrated. So for textured light absorbing materials, photon in/out-coupling is overall optimized to improve the performance of twojunction devices. Furthermore, Wang et al.99 have investigated the effects of conformality and thickness of the PSK cladding on the c-Si bottom-cell (Fig. 5(c)). They have demonstrated that the conformal PSK layer (angle difference of 0°) with suitable thickness ( $\sim$ 700 nm) will achieve the maximum tandem PCE.

### Review

To study the optimal value of pyramidal size in the PSK/c-Si TSC, Qarony *et al.*<sup>105</sup> have shown through simulations (Fig. 5(d1 and d2)) that the quantum efficiency is progressively increased with the pyramid-scale from flat to 1.5  $\mu$ m and a fixed period-to-height ratio. Previously, Ba *et al.*<sup>98</sup> have revealed (see Fig. 5(e)) that the optimal parameters of the top and bottom pyramids in the PSK/c-Si TSC are approximately 1  $\mu$ m and 3  $\mu$ m, respectively. The discrepancy lies in the fact that Qarony *et al.*<sup>105</sup> have simply considered c-Si of infinite thickness, which implies that there is no factor of bottom roughness, while the study in ref. 98 is very relevant to the actual condition and the conclusion is more universal and accurate. The above argument suggests that only suitable sizes of large-scale pyramids can be understood as textures with a robust light trapping effect in the PSK/c-Si TSC.

### 4.3. Experimental optimization of electrical properties

For the case of the single junction and without any special optical structure, many literature studies<sup>110–114</sup> have reported that the better the mirror-like effect of the PSK, the better the

electrical performance of the device. Since the light absorption capability of planar PSK is mainly determined by the bandgap, the improvement of PCE with the same bandgap basically depends on the electrical gain. In addition, the substrate undulation has a large impact on the growth of the PSK crystals, so for the PSK on pyramid-textured surfaces, their electrical optimization is urgently required. Various groups<sup>44-50</sup> have focused their research on two aspects, the transport layer and the PSK light-absorbing active layer.

For p–i–n conformation devices, the textured inorganic hole transport layer (HTL) interface has many chemically active sites and carrier recombination defects, which severely limit the PCE enhancement of the PSK/c-Si TSC.<sup>115</sup> To overcome this challenge, Zhumagali *et al.*<sup>50</sup> have employed organometallic dye<sup>116</sup> (N719) molecules to passivate the surface traps of NiO<sub>x</sub>, which eventually led to an increase in the TSC PCE from 23.5% (without N719) to 26.2% (with N719). To further investigate the passivation mechanism, they have calculated using density functional theory (DFT) (Fig. 6(a1)) that the carboxyl groups of



**Fig. 6** Electrical optimization of the planarized structure during the experiments. For the transport layer: (a1) 3D charge density differences of the N719 molecule interfacial binding modes. On the left is the binding of N719 and NiO<sub>x</sub>, and on the right is the binding of N719 and PSK. Reproduced with permission,<sup>50</sup> copyright 2021, John Wiley and Sons. (a2) Diagram of the self-assembly process. The magnified region shows the interaction of  $C_{60}$ -SAM molecules with Nb<sub>2</sub>O<sub>5</sub>. (a3) TRPL decay of the corresponding architecture. On the bottom left is a schematic of the structure under the 532 nm excitation condition. Reproduced with permission,<sup>44</sup> copyright 2021, The Royal Society of Chemistry. For the PSK light-absorbing active layer: (b1) schematics of carrier generation, diffusion and drift in the pyramid-textured surface. h<sup>+</sup>, holes; e<sup>-</sup>, electrons. The shaded part of the slanted line is the drift dominant region of PSK, the cyan part in the middle is the diffusion dominant region of PSK, and red areas represent charge generation regions. Reproduced with permission,<sup>47</sup> copyright 2020, The American Association for the Advancement of Science. (b2) Scanning electron microscopy (SEM) image of the PSK coverage on c-Si surfaces and the passivation mechanism of the PhenHCl molecule at the PSK grain boundaries and top-surfaces. The insets represent the passivation model for three surfaces of the PhenHCl molecule's electronic binding. Reproduced with permission,<sup>48</sup> copyright 2021, Elsevier. Electrical optimization of the conformal structure. (c1) Non-optimized cross-sectional SEM image of the covered PSK. Reproduced with permission,<sup>53</sup> copyright 2018, Springer Nature. (c2) SEM image showing the PSK, CsBr, and the HTL. Reproduced with permission,<sup>56</sup> copyright 2021, John Wiley and Sons.

N719 can form -COONi and -COOPb at the interface, indicating a prominent electrical-bridging effect of N719 on the texture, which is the root cause of the PCE boost. Organic HTLs (PTAA, 2PACz, MeO-2PACz, etc.) unfold at textured interfaces with good molecular-level dispersion (inorganic HTLs are molecularly integrated particles),<sup>15,45,48,57</sup> thus their defect states are greatly reduced. Especially for some HTLs that are single molecular layers, their attachment to the textured surface is ordered and dense. Al-Ashouri et al.15 have demonstrated that the self-assembled monolayer (SAM) material (Me-4PACz) has robust hole extraction properties. For n-i-p devices, the textured side is the electron transport layer (ETL). To overcome the difficulties of electrical transport in conventional ETLs, Aydin et al.<sup>44</sup> (Fig. 6(a2)) have anchored C<sub>60</sub>-SAM on the Nb<sub>2</sub>O<sub>5</sub> surface. The time-resolved photoluminescence (TRPL) results (Fig. 6(a3)) have exhibited a decrease in luminescence lifetime from 140 ns (without anchored C<sub>60</sub>) to 57 ns (with anchored  $C_{60}$ ), confirming the enhanced charge extraction properties of the self-assembled layer at the pyramid-textured interface.

To improve the optoelectronic properties of the PSK layer, Hou et al.47 (Fig. 6(b1)) have enhanced the electrical stability of the PSK by adding trioctylphosphine oxide (TOPO) and effectively suppressed the non-radiative recombination. They have also tripled the depletion width at the valley of the c-Si pyramid, conquering the challenge of charge collection in micrometerthick PSK. The carrier diffusion length has been further increased by immobilizing a self-limiting passivator (1-butanethiol) on the PSK surface. The PCE of the TSC has been finally improved from 24% to 26% after the PSK optimization. Isikgor et al.48 (Fig. 6(b2)) have considered the severe back-transfer recombination and the high number of PSK activity defects caused by c-Si textured surfaces and used phenformin hydrochloride (PhenHCl) molecules with electron-rich and electronpoor functional groups to perform the electrical refinement of the PSK grain boundaries as well as the top-surface. The PCE of the TSC before and after passivation was 25.4% (without PhenHCl) and 27.4% (with PhenHCl), respectively, achieving a tremendous enhancement.

It should be noted that the reported highest laboratory PCE so far of the PSK/c-Si TSC with the conformal structure is still lower than that of the flat structure. The intrinsic reasons may be attributed to the PSK nucleation process and textured transport layers (ETL and HTL). For the conformal PSK active layer, the drawbacks (many pinholes, poor crystallization, and lack of passivation at grain boundaries) are caused when the grains grow independently of each other due to the lack of filmforming forces (e.g., centrifugal forces for the one-step spincoating,<sup>15–19</sup> propulsion forces for the blade-coating,<sup>45</sup> etc.). As shown in Fig. 6(c1), the PSK covering the top of the pyramid is not smooth, but a raised hill, which can cause electrical losses such as non-radiative43,117-122 recombination. For the textured ETL and HTL, excessive undulation can lead to non-uniform coverage of the transport layer materials or even poking through, which can eventually lead to low PCE and poor repeatability of the device. Therefore, a direct study of the conformal structure of the dual-textured PSK is bound to face many challenges. It is commendable that Li et al.56 have broken

the 2018 record of  $25.2\%^{53}$  for the conformal structure by introducing a gradient PSK absorber (*via* CsBr) and adjusting the thickness of the HTL to achieve 27.48% PCE (Fig. 6(c2)) (without electrical optimization, PCE = 25.17%). This optimization of the PSK light-absorbing active layer (matching energy levels) and HTL improves the charge transport, which fully supports our view. In the future, as the electrical optimization technology matures, it will certainly give guidance to the optimization route of the conformal PSK/c-Si TSC and achieve robust photon-to-electron conversion capability.

## 5. Metrics for practical applications of the PSK/c-Si TSC

Considering the promising development of the PSK/c-Si TSC with high PCE potential, the problems of large-scale manufacturing, stability issues, and bifacial properties cannot be avoided in order to realize industrialization and application. A large number of literature reports are available in these fields, and below we review the most representative achievements.

#### 5.1. Large-scale manufacturing

Currently, industrialized c-Si solar cells can easily reach  $21 \times 21$ cm<sup>2</sup> (PCE 23.5%),<sup>123</sup> while the maximum area of single-junction PSK solar cells is only 63.98 cm<sup>2</sup> (PCE 20.1%),<sup>124</sup> and it is also formed by a module of 12 solar cells, so the large-scale production of the PSK/c-Si TSC is bound by the area of the PSK. As shown in Table 1, the active area of most of the PSK/c-Si TSCs reported in the literature is about  $1 \text{ cm}^2$  (or even smaller); high PCE and large area seem to be incompatible, which makes the industrialization of the PSK/c-Si TSC very tough. To investigate the feasibility issues of large-scale manufacturing of the TSC, Zheng et al.<sup>39</sup> (Fig. 7(a1)) designed a metal grid electrode on top of the TSC based on a homojunction bottom-cell, achieving an excellent FF (76% for the forward scan and 78% for the reverse scan) and enabling a steady-state PCE of 21.8% on an area of 16 cm<sup>2</sup>. Besides, Kamino et al.<sup>42</sup> (Fig. 7(a2)) successfully solved the large-scale challenge of the top electrode by screen printing low-temperature silver paste to realize metallization on the surface of the PSK top-cell when the bottom-cell was a heterojunction. The preparation process was also compatible with the front metal finger of the c-Si industry, achieving a steady-state PCE of 22.6% on an area of up to 57.4 cm<sup>2</sup>, which is the largest area PSK/c-Si TSC reported to date. More efforts are required from researchers in order to accelerate the commercialization of the PSK/c-Si TSC (from small area devices to large-scale production with high PCE). Luckily, Oxford PV launched a 250 MWp mass-production project of the PSK/c-Si TSC in 2020, and its TSC product is expected to be put on the market in early 2022.125

#### 5.2. Stability issues

Despite the high PCE potential of the PSK/c-Si TSC, the lifetime discrepancy between the c-Si bottom-cell and the PSK top-cell also limits the development of the TSC, and the stability of the PSK has become a stumbling block for industrialization.



Fig. 7 Metrics for practical applications of the PSK/c-Si TSC, including large-scale manufacturing, stability issues, and bifacial properties. (a1) Picture and J-V curves (forward scan and reverse scan) of the TSC with an area of 16 cm<sup>2</sup>. Reproduced with permission,<sup>39</sup> copyright 2018, American Chemical Society. (a2) Object photograph (left) of the TSC prepared by low-temperature screen-printed metallization, and the measured J-V curves (right) at an aperture area of 57.4 cm<sup>2</sup>. Reproduced with permission,<sup>42</sup> copyright 2019, American Chemical Society. (b1) Evolution curves of the PSK bandgap at different ratios of Cl/(l + Br + Cl). According to the ratios of Cs and Br, they are simplified to Cs25Br15, Cs25Br30, and Cs25Br40, such as FA<sub>0.75</sub>Cs<sub>0.25</sub>Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>3</sub> denoted as Cs25Br15. The dotted line is the demarcation between the single phase and double phase. (b2) XRD zoomed-in view of the (100) peak; shifting and splitting indicate a transition from the single phase to the double phase in a triple-halide alloy with increasing Cl/(l + Br + Cl) ratios. Here, the host PSK is Cs25Br40. (b3) Evolution curves of the lattice constant of the host PSK with increased Cl content. Reproduced with permission,<sup>36</sup> copyright 2020, The American Association for the Advancement of Science. (b4) Long-term stability studies under illumination and an N<sub>2</sub> environment without encapsulation. PEA, phenethylammonium; SCN, thiocyanate. Reproduced with permission,<sup>25</sup> copyright 2020, The American Association for the Advancement of Science. (c1) Photographs of the

The stability issues of the PSK can be broadly divided into two aspects: (1) chemical instability: the PSK material reacts easily with water and oxygen molecules in the ambient environment;126-129 (2) physical instability: PSK has low dissociation energy (e.g., MAPbI<sub>3</sub> 0.27 eV<sup>130,131</sup>), the A-site<sup>132</sup> or X-site<sup>133,134</sup> ions are prone to diffusion and migration, and phase segregation (Hoke effect<sup>135</sup>) occurs easily by forming various secondary phases under illumination conditions.136-144 For chemical stability, the encapsulation of PSK devices can effectively improve the tolerance to moisture and oxygen and avoid the causative factor of PSK crystal dissociation.145-150 However, it has been an insurmountable problem for physical stability, because the lattice of PSK is not stable, temperature alone can induce phase changes,151,152 and ion diffusion and migration occur all the time (e.g., the activation energy of  $I^-$  for vacancy-assisted migration is only 0.6 eV133). Moreover, several studies138,143 have shown that ion migration may be one of the causes of lightinduced phase segregation in wide-bandgap mixed halide PSK, indicating that the physical dissociation factors are not independent but complementary.

In order to solve the contradiction between the PSK bandgap and halide phase segregation, Xu et al.<sup>36</sup> (Fig. 7(b1)) found that although Br plays the main role in bandgap tuning, the addition of an appropriate amount of Cl can widen the bandgap. This finding indicates that the addition of Cl makes it possible to achieve a wide bandgap, while the Br content can be appropriately reduced, attenuating the phase segregation from the source of the mixed halides. The intrinsic mechanism was revealed by X-ray diffraction (XRD) characterization (Fig. 7(b2)). Xu et al.<sup>36</sup> observed that a small increase in Cl/(I + Br + Cl) could shrink the lattice of PSK but still maintain a single phase, and that the bandgap reduction at high Cl content was caused by phase segregation into two PSK phases. The lattice constant of the host PSK (Fig. 7(b3)) expands (the diffraction peak shifts to a lower angle) with the appearance of the phase-segregated PSK, which agrees with the observed narrowing of the bandgap. In addition, Liang et al.<sup>140</sup> showed that potassium in KI can be used to effectively suppress light-induced phase segregation and also improve the crystallinity of wide-bandgap mixed halide PSK. To further improve the physical instability due to diffusion, Kim et al.25 (Fig. 7(b4)) made a significant improvement in the PV performance by introducing an anion-engineered twodimensional (2D) additive ( $PEA(I_{0.25}SCN_{0.75})$ ) at the threedimensional (3D) PSK grain boundaries, maintaining 80% of the initial PCE (20.7%) even after 1000 hours of continuous illumination. The molecular-level mechanism of the enhanced stability in this case originates from the encapsulation effect of the 2D additive, which to some extent blocks the ion diffusion and migration and inhibits the dissociation of the material itself. Further, Li *et al.*<sup>56</sup> achieved a great breakthrough in stability by depositing a CsBr thin layer, and the PCE of the conformal structure decreased by only 1.41% (absolute) at 10 488 hours under a nitrogen environment. Although these studies above are significant for improving the stability of the PSK/c-Si TSC, they still cannot meet the requirements of industrial fabrication and commercialization, and solving the stability issues of the PSK top-cell is still one of the main topics for future research.

#### 5.3. Bifacial properties

Unlike full-back surface electrodes, the backside of the bifacial PSK/c-Si TSC is formed with the grid finger (Fig. 7(c1)), which is capable of receiving scattered and reflected light from the environment for power generation in addition to normal power generation on the front side.<sup>153-157</sup> As shown in Fig. 7(c2), De Bastiani et al.46 found through experiment that the maximum increase in power generation density (PGD) can reach about 7.5 mW  $\mathrm{cm}^{-2}$  (bandgap 1.59 eV) as the backside irradiance increases from 0 to 100 mW cm<sup>-2</sup> in the case of 1 sun front illumination. And their simulation results for Seattle (Fig. 7(c3)) also show a maximum increase in annual energy yield of nearly 50% with increasing albedos (from 0% on monofacial case to 88% on snow) (1.59 eV bandgap from approximately 270 to 400 kW h  $m^{-2}$ ), profoundly revealing that the backside power generation of the PSK/c-Si TSC is not to be underestimated. According to their results, the 1.68 eV bandgap is the optimal bandgap for the monofacial case, and the optimal bandgap of the bifacial TSC becomes narrower as the albedos increase. Previously, Onno et al.158 obtained the dependence of the optimal bandgaps and albedos of the top-cell by simulation (Fig. 7(c4)), and they found that the points shift downward in cloudy (blue) weather, indicating that the bandgap can be appropriately narrow when there is insufficient light (fixed albedo), and these findings can provide a quick and powerful reference for experiments and simulations. However, the results of ref. 158 are ideal models for current matching, and according to Boccard *et al.*,<sup>159</sup> the current shunting can have a huge impact on the FF of the TSC, which means that the current matching model is restricted. To obtain more accurate results, Du et al.<sup>160</sup> observed that the bifacial solar cell would generate additional  $I_{Alb}$  due to the presence of albedo (Fig. 7(c5)), and nevertheless the short-circuit current of the TSC would always be limited by the minimum one, which means that the energy yield would no longer increase after a certain range of albedo. Moreover, they

TSC rear (top) and front (bottom) metal contacts. (c2) Power generation density (PGD) of the bifacial TSC with different bandgaps when the front is under 1 sun conditions. (c3) Annual energy yield (EY) of the 2T TSC under different albedos and bandgaps in Seattle. The value of the horizontal coordinate represents the albedos. Reproduced with permission,<sup>46</sup> copyright 2021, Springer Nature. (c4) Statistical plot of the dependence of the effective albedo and the optimal bandgap of the top-cell. Ten data points are taken daily, from 08:30 to 17:30. The dashed line is the static sensitivity analysis at AM 1.5 G irradiance (not considering shading, spectral effects, temporal irradiance variation, *etc.*). The inset integrates the results of a day into 1 data point. The blue data points in the graph represent cloudy weather, and the other dark data points represent clear weather. The color change only represents the difference in scenes (which are eventually summarized as effective albedo), so no distinction is made here. Reproduced with permission,<sup>158</sup> copyright 2020, Elsevier. (c5) Schematic diagram of *E*-field distribution and current generation for monofacial (left) and bifacial (right) TSCs. (c6) PCE losses due to current mismatch for different bandgaps and variable albedos.

### Review

innovatively propose a feasible method of current matching loss (CML) based on the energy balance principle and provide an optimization scheme from the source to reduce the impact of CML on the performance improvement of the bifacial TSC. As shown in Fig. 7(c6), their results reveal that the wider the PSK top-cell bandgap, the more the CML when the albedo is greater than 18.1%, and the PCE loss even reaches 14% when the albedo reaches 64% (bandgap 1.75 eV). As the c-Si PV industry has been gradually moving toward the bifacial module, the industrialization direction of the PSK/c-Si TSC will certainly realize bifacialization for higher comprehensive power generation efficiency.

### 6. Summary and outlook

c-Si solar cells have dominated the residential PV market for more than 20 years. This review points out that single-junction c-Si solar cells are approaching the ceiling (Shockley–Queisser limit 29.4%<sup>7</sup>), and the development of two-junction solar cells has become imperative. In the past 6 years, although the progress of these three types of solar cells (PSK/c-Si, PSK/CIGS, and PSK/PSK) has been very rapid, they are still very far from theoretical limits. The key to improving the PCE of the PSK/c-Si TSC is how to extend the superstrate advantage of PSK on conductive glass to Si wafers. For PSK/CIGS and PSK/PSK research, in addition to addressing the topics discussed in Section 2, the development of flexible tandem devices may be a promising direction.

There are currently five options reported in the literature for the preparation of PSK on silicon substrates: low-cost spincoating, large-area blade-coating and slot-die coating, facile physical stacking, and excellent conformal co-evaporation + solution. It is worth noting that while co-evaporation + solution is suitable for substrates with various roughnesses, the complex two-step approach can result in high cost and low performance of the PSK/c-Si TSC. In order to obtain PSK films with large area, excellent quality and robust stability, it is essential to explore new simple one-step solution-based or vapor-based deposition schemes for conformal structures. The one-step solution-based method may alter the viscosity of the precursor solution through additives or solvent engineering to achieve confinedspace growth161,162 of PSK and conformal coverage. Whether as an additive or a primary solvent, the ambient air-preparation of environmentally friendly and viscous ionic liquid<sup>163</sup> might be a viable option. The difficulty of the one-step vapor-based technology lies in the treatment with organic halide sources and the control of the components' atmosphere.

We have calculated PCEs of 31.4%, 30.6%, 31.0%, and 28.5% based on the best experimental EQE spectra of the conformal, flat, and planarized structures, and mechanical stacking in the literature, showing that the conformal structure has excellent spectral response. This is consistent with the conclusion of numerous optical simulations that the textured structure will cause more optical coupling and resonance absorption, reflecting the conformal structure specificity. Regarding the low experimental PCE of the conformal structure, the electrical optimization of the PSK active layer and the transport layer can

improve the PCE very significantly (up to 2.31% (absolute) PCE enhancement). Therefore, we conclude that electrical passivation and energy level alignment are compulsory ways to improve PCE, and the search for special molecular groups with robust passivation, carrier extraction, and transport is the following work. In addition, the light parasitic absorption of textured functional layer materials (interconnected, transport, and TCO layers) is not negligible, but its modification needs to be carried out under the premise that the electrical performance is guaranteed; even HTL- and ELT-free PSK/c-Si TSCs might be realized in the future.

Finally, the review summarizes the application metrics of the PSK/c-Si TSC. The current preparation scheme for the largest area of PSK/c-Si TSC is spin-coating, which can reach 57.4 cm<sup>2</sup> and the PCE can reach 22.6%.42 To achieve larger area and higher PCE, slot-die, blade-coating and vacuum evaporation methods may be reliable options. Moreover, through the preparation of a gradient PSK layer (via CsBr), the stability can still be guaranteed after 10 488 hours under a nitrogen atmosphere.56 With respect to the PSK/c-Si TSC's outdoor stability, the optimization means of single-junction PSK solar cells can be followed, such as alkali metal ion addition, low-dimensional PSK interfaces, etc. For the study of bifacialization, although the experiment is still at the beginning stage, the calculated results show that the energy yield can be improved by about 50%,46 and the CML160 with outstanding significance can guide us to adjust the bandgap to achieve matched absorption of bifacial spectra. Since the actual solar spectrum and effective albedo are always changing, the current mismatch must be minimized before PSK/c-Si TSC fabrication and module installation. Based on the breakthroughs in the large-scale manufacturing, stability, and bifacial properties of the PSK/c-Si TSC, we believe there are no insurmountable challenges in reaching above 30% module PCE in the future.

### Author contributions

Chao Gao: conceptualization, investigation, methodology, validation, writing – original draft. Daxue Du: investigation. Dong Ding: investigation. Feiyang Qiao: investigation. Wenzhong Shen: resources, supervision, project administration, funding acquisition.

## Conflicts of interest

The authors declare no conflict of interest.

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