

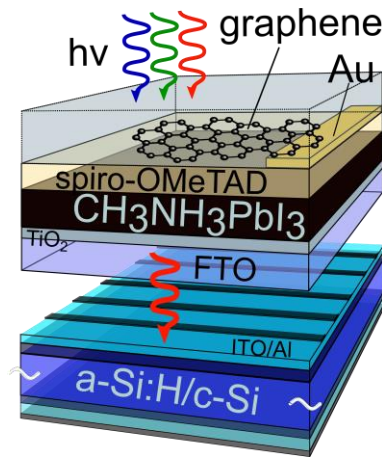
Perovskite Solar Cells with Large-Area CVD-Graphene for Tandem Solar Cells

Felix Lang^{*}, Marc A. Gluba, Steve Albrecht, Jörg Rappich, Lars Korte, Bernd Rech, and
Norbert H. Nickel

Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium
Photovoltaik, Kekuléstr. 5, 12489 Berlin, Germany.

ABSTRACT: Perovskite solar cells with transparent contacts may be used to compensate thermalization losses of silicon solar cells in tandem devices. This offers a way to outreach stagnating efficiencies. However, perovskite top cells in tandem structures require contact layers with high electrical conductivity and optimal transparency. We address this challenge by implementing large area graphene grown by chemical vapor deposition as highly transparent electrode in perovskite solar cells leading to identical charge collection efficiencies. Electrical performance of solar cells with a graphene-based contact reached those of solar cells with standard gold contacts. The optical transmission by far exceeds that of reference devices and amounts to 64.3 % below the perovskite band gap. Finally, we demonstrate a four terminal tandem device combining a high band gap graphene-contacted perovskite top solar cell ($E_g=1.6$ eV) with an amorphous/crystalline silicon bottom solar cell ($E_g=1.12$ eV).

1 TOC GRAPHIC.



2

3

4 Hybrid perovskite methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) attracts ever-growing interest
5 for use as a photovoltaic absorber.¹ Only recently, Jeon et al. demonstrated the great potential of
6 this material in a single-junction solar cell with an efficiency of 18%².

7 Moreover, the low sub band gap absorption³⁻⁶, increasing steeply to about $\alpha \approx 10^4 \text{ cm}^{-1}$ at
8 600 nm⁷, enables semi-transparent perovskite solar cells to pre-filter the solar spectrum for low
9 band gap absorbers in multi-junction devices. In particular, the combination with crystalline
10 silicon (c-Si), which has a band gap of 1.12 eV at room temperature⁸, is a promising route to
11 circumvent thermalization losses in conventional photovoltaic energy conversion. By these
12 means, conversion efficiencies beyond the Shockley-Queisser-limit are anticipated for
13 perovskite/silicon tandem devices.^{9,10}

14 Realizing a perovskite/silicon tandem design requires electrodes, which must be gently deposited
15 onto organic layers of the hybrid perovskite top cell while being particularly transparent in the IR

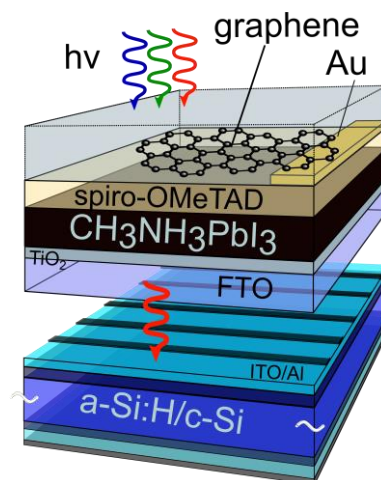
1 spectral regime. Due to the unique optoelectronic properties of graphene this material is the clear
2 choice to tackle this challenge. Electrodes based on graphene combine excellent optical
3 transmission (T) of 97.4 % with a sheet resistance of 100 Ω/sq ¹¹.

4 Apart from graphene, different strategies to contact the perovskite top cell have been proposed
5 before, most of them suffering from a considerable amount of parasitic absorption at long
6 wavelengths. Initial attempts based on 20 nm thin semi-transparent aluminium contacts achieve
7 optical transmission of only 30 %. ¹² Promising alternatives such as lamination of a silver
8 nanowire (AgNW) mesh ^{10,13}, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
9 (PEDOT:PSS) layers ¹⁴, or carbon nanotube networks ¹⁵ have been proposed recently. Currently,
10 the best performing perovskite/silicon tandem device with an energy conversion efficiency of
11 17.0 % ¹⁰ is based on AgNW electrodes. However, the maximum transmission of such electrodes
12 is small compared to graphene and varies between 83 and 89.5 %, only. ^{16,17}

13 On the other hand, conventional transparent conductive oxides are optimized for spectral
14 transmission but cannot be directly deposited onto the perovskite top cell. Ion bombardment
15 during sputter deposition deteriorates the topmost hole-transport layer. Minimizing the damage
16 of its organic material requires additional buffer layers and a meticulous control of the deposition
17 process. ⁹ These buffer layers and their defective interfaces cause substantial current losses. ⁹

18 While previous electrodes are limited either by electro-optical performance or processability, we
19 demonstrate that graphene is a suitable contact material and is fully compatible to solution
20 processing of perovskite solar cells. For this purpose, large-area graphene grown by chemical
21 vapor deposition (CVD) ^{18,19} is transferred onto a perovskite solar cell consisting of the layer

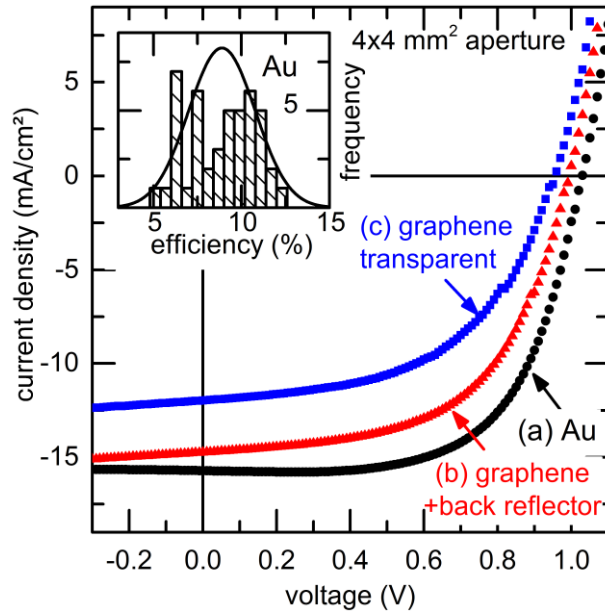
1 sequence glass/SnO₂:F/TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD. The latter abbreviates the hole
2 conductor 2',7,7'-tetrakis-(N,N-di-4-methoxy-phenyl-amino)-9,9'-spirobifluorene. Figure 1
3 shows a sketch of the graphene based perovskite solar cell and the intended four terminal tandem
4 device. It is important to note that the transfer process did not deteriorate the interface and bulk
5 properties of the underlying hole conducting layer. Structural characterization of the used single
6 layer graphene revealed the presence of wrinkles, nanoscale holes, and grain boundaries.
7 However Raman backscattering revealed a negligible graphene D mode compared to the G and
8 2D resonances. In a recent report ²⁰ on graphene contacts in perovskite solar cells an additional
9 PEDOT:PSS layer was incorporated to enhance adhesion of graphene to the spiro-OMeTAD
10 layer and to introduce field-effect doping in the graphene to lower the sheet resistance. Our data
11 clearly shows that the PEDOT:PSS layer can be omitted, which renders the device structure less
12 complex and results in a higher transparency. This is an important aspect for tandem solar cells.
13 Details on the preparation of the solar cells can be found in the experimental section.



14

1 **Figure 1.** Simplified sketch of a four terminal tandem solar cell consisting of a graphene based
2 perovskite top solar cell and an amorphous/crystalline silicon bottom solar cell. Figure not true to
3 scale. The illumination direction of the perovskite top cell may be reversed.

4 In order to demonstrate the successful integration of graphene into the perovskite solar cell we
5 compare the current-voltage (JV) characteristics of a perovskite solar cell with a graphene
6 contact to a reference device containing a gold electrode (Fig. 2). Both solar cells were fabricated
7 and analyzed side-by-side on the same substrate, to ensure comparability. The JV measurements
8 are directly compared in reverse direction (from positive to negative bias). For clarity, the
9 commonly observed hysteresis between forward and reverse measurements^{21,22} is omitted in
10 Fig. 2. The JV curves from forward and reverse measurements can be found in the
11 supplementary information (Fig. S1). The electrical characteristics of the solar cells are
12 summarized in Table 2.



13

1 **Figure 2.** Current density-voltage characteristics of perovskite solar cells measured under
 2 AM1.5G conditions. (a) Reference solar cell with 80 nm Au contact. (b) Perovskite solar cell
 3 with graphene contact. The device was illuminated from the graphene side and a white diffusive
 4 reflector was used at the glass/SnO₂:F side. (c) Semi-transparent perovskite top cell with
 5 graphene contact illuminated from the glass/SnO₂:F side (without back reflector). The inset
 6 shows a histogram of measured solar cell efficiencies with Au contacts.

| Cell Type | η (%) | V _{oc} (V) | I _{sc} (mA/cm ²) | FF (%) |
|--|------------|---------------------|---------------------------------------|--------|
| (a) single, Au contact | 10.2 | 1.03 | 15.75 | 62.9 |
| (b) single, Graphene contact and back reflector | 8.3 | 0.99 | 14.75 | 56.6 |
| (c) top cell for tandem devices, Graphene contact | 6.2 | 0.90 | 12.56 | 55.0 |

7

8 **Table 1.** Parameters of single perovskite solar cells (a, b) and top perovskite solar cell for use
 9 in tandem devices (c).

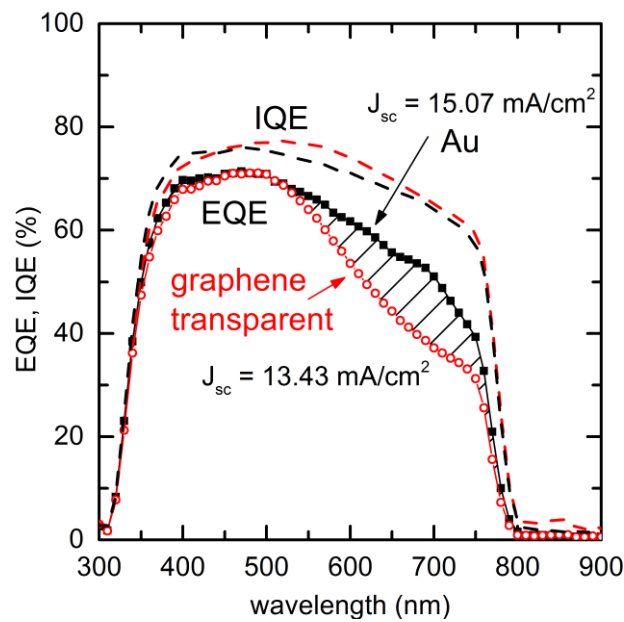
10 The black circles in Fig. 2 show the typical JV curve of a reference perovskite solar cell with
 11 standard Au contact. To check the reproducibility of the cell preparation, 42 cells were processed
 12 and the histogram of their efficiencies is plotted in the inset of Fig. 2. A mean value of $\eta = 8.9\%$
 13 is obtained with the highest efficiency amounting to $\eta = 12.4\%$. The power conversion
 14 efficiency of the reference cell prepared concurrently with the graphene/perovskite cell
 15 amounted to $\eta = 10.2\%$.

16 Since reflection at the gold contact effectively doubles the light path, we compare this
 17 reference solar cell to a graphene-contacted device with a Lambertian back reflector (red
 18 triangles in Fig. 2). The semi-transparent cell was illuminated from the graphene side with a

1 white paper used as reflector at the glass side. The open circuit voltage amounts to $V_{OC} = 0.99$ V,
2 which is close to the V_{OC} of the Au reference solar cell ($V_{OC} = 1.03$ V). This clearly shows that a
3 graphene contact can be successfully integrated in perovskite solar cells without deteriorating the
4 device. Furthermore, the very similar V_{OC} shows that no substantial band offsets are introduced
5 by the graphene contact. Remarkably, this was accomplished without the need for a buffer layer
6 that promotes adhesion and field-effect doping.²⁰ Here, adhesion and intimate contact of
7 graphene on spiro-OMeTAD is ensured by Van-der Waals forces.

8 The power conversion efficiency of the graphene/perovskite solar cell shows a somewhat
9 lower value of $\eta = 8.3$ %. This is due to (i) a small contribution to the efficiency loss results from
10 the short circuit current, J_{SC} , which decreases from 15.75 mA/cm² for the reference solar cell to
11 14.75 mA/cm² of the device with the graphene contact. This is not an issue of charge collection
12 at the graphene electrode. In fact, the reduced J_{SC} is due to the lower photogeneration as result of
13 the poor Lambertian back reflector. It has to be noted that also the entire device optic changed
14 due to the switched illumination direction. Especially, parasitic absorption of the spiro-OMeTAD
15 layer in the wavelength range from 300 to 450 nm becomes relevant since the device was
16 illuminated from the graphene side. Moreover (ii) a reduction of the fill factor (FF) from 63 % on
17 the Au reference to 57 % with graphene electrode contributes to the efficiency loss. A detailed
18 analysis of the device parameters reveals an increase in series resistance from $R_S = 10.7$ Ω cm² in
19 case of the Au electrode to 12.3 Ω cm² for the device with graphene electrode. R_S is estimated
20 from the JV curves using $R_S = \left. \frac{dV}{dJ} \right|_{V=V_{oc}}$. This increase in R_S is a direct consequence of the
21 increase in electrode sheet resistance from $\rho = 1.63$ Ω /sq to $\rho = 350$ Ω /sq for Au and graphene
22 contacts respectively.

1 The blue squares in Fig. 2 show the JV characteristics of the graphene/perovskite solar cell
2 when illuminated from the glass/SnO₂:F side without a back reflector. This device geometry will
3 be used later to demonstrate a perovskite/silicon tandem device. In this case, the light passes the
4 solar cell only one time and therefore, the short circuit current decreases to $J_{SC} = 12.56 \text{ mA/cm}^2$.
5 Hence, the efficiency of the semi-transparent perovskite top cell amounts to $\eta = 6.2 \%$ when
6 used in a four-terminal tandem device.



7
8 **Figure 3.** External (EQE) and internal quantum efficiency (IQE) spectra. The open red circles
9 and full black squares correspond to the measured EQE of the graphene and Au contact,
10 respectively. The red and black dashed lines correspond to the calculated IQE for graphene and
11 Au contacts, respectively. The devices were illuminated from the glass/SnO₂:F side.

12 To substantiate the identical charge collection at the graphene contact with respect to the gold
13 electrode the spectral response of both cells was measured. Figure 3 shows external (EQE) and
14 internal (IQE) quantum efficiency measurements for the semi-transparent graphene/perovskite
15 solar cell and the Au contacted reference cell. Both samples were illuminated from the

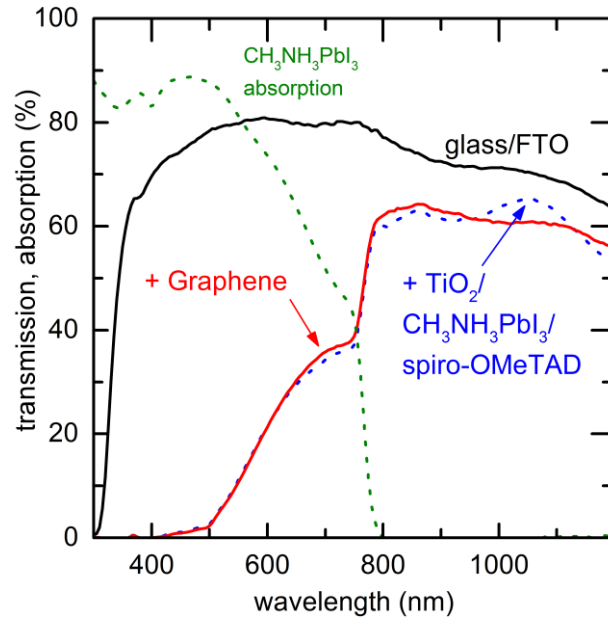
1 glass/SnO₂:F side. The EQE measured on the Au reference (solid squares in Fig. 3) reaches
2 values of up to 71 % and an integrated current of 15.07 mA/cm². This integrated J_{SC} matches J_{SC}
3 obtained from JV measurements (see Fig. 2). The EQE of the semi-transparent
4 graphene/perovskite cell is reduced for wavelengths above 600 nm (open circles in Fig. 3). In
5 this spectral regime the optical absorption in the perovskite starts to decrease and a considerable
6 amount of light passes through the device without being absorbed. In a tandem device the
7 transmitted light generates charge carriers in the bottom cell. Hence, changing the thickness of
8 the perovskite absorber allows to adopt the transmittance of the top cell to the spectral response
9 of the bottom cell.

10 The IQE is calculated from the reflection, R(λ), and transmission, T(λ), of the perovskite cell
11 according to ²³

$$12 \quad \text{IQE}(\lambda) = \frac{\text{EQE}(\lambda)}{1 - R(\lambda) - T(\lambda)}. \quad (1)$$

13 The IQE of the graphene/perovskite solar cell (red dashed line in Fig. 2) reaches a maximum of
14 77.3 % at 520 nm. In comparison, the device with the Au contact shows a maximum of 76.1 %,
15 only. Hence, graphene contacts show identical charge collection efficiency and light
16 management even at long wavelengths.

17 In addition to the equal charge collection, the quantum efficiency of the semi-transparent
18 graphene/perovskite solar cell suggests an optical benefit from using a graphene electrode. To
19 elucidate the optical performance of this contact, the parasitic absorption within the
20 graphene/perovskite device is analyzed in detail. For this purpose, diffuse transmission,
21 reflection, and absorption of each individual layer are investigated.



1
 2 **Figure 4.** Transmission spectra of glass/SnO₂:F (solid black line), the perovskite top solar cell
 3 layer stack glass/SnO₂:F/TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD (dotted blue line), and of
 4 glass/SnO₂:F/TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD/graphene/support (solid red line). Absorption
 5 of CH₃NH₃PbI₃ on glass (dotted olive line).

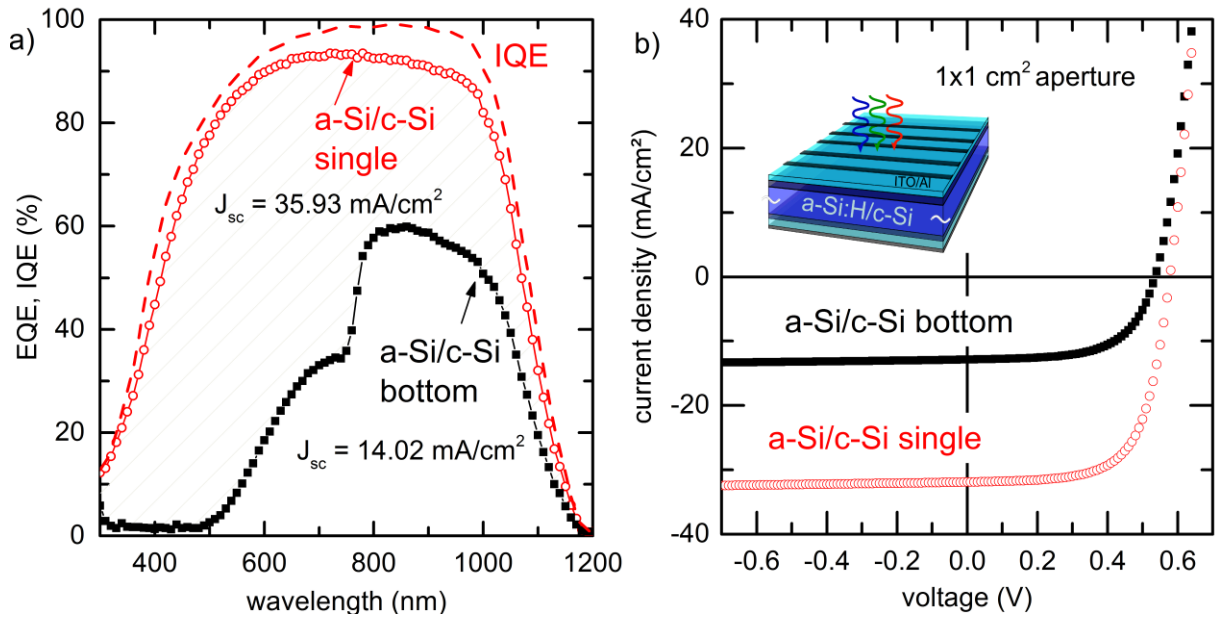
6 Figure 4 shows the optical absorption of the CH₃NH₃PbI₃ perovskite absorber on glass (olive
 7 dashed line) and the transmission of the glass/SnO₂:F substrate (solid black line). The perovskite
 8 absorber shows a broad absorption tail from over 80 % absorption at a wavelength of $\lambda \approx 500$ nm
 9 to around 40 % at $\lambda \approx 750$ nm. The SnO₂:F reaches a maximum transmission of 80 % at around
 10 600 nm. At longer wavelengths the transmission decreases to about 65 % due to free carrier
 11 absorption.²⁴

12 Although the absorption of the perovskite is low in the sub band gap region, the transmission of
 13 the device prior to the graphene transfer (dotted blue line in Fig. 4) is reduced to 60 %, only. This
 14 is due to enhanced reflection at the spiro-OMeTAD/air interface.

1 To evaluate the optical impact of the graphene contact a direct comparison between the
2 transmission of the perovskite solar cell stack with and without graphene is of particular interest.
3 The red solid line in Fig. 4 shows the transmission of the complete device structure including
4 graphene and its polymer-support. Remarkably, an increase of the absolute transmission of
5 around 2 %, compared to the sample without graphene/support is observed for
6 $650 < \lambda < 950$ nm. This effect is due to a reduced reflection at the spiro-
7 OMeTAD/graphene/support versus the spiro-OMeTAD/air interface. A decrease in transmission
8 observed for $950 < \lambda < 1130$ nm is due to increased reflection, caused by the same interference
9 effect. This anti-reflection effect of the graphene contact including its polymer support enhances
10 the optical transmission of the semi-transparent perovskite solar cell. These beneficial effects
11 even predominate the absorption at the graphene contact itself, since the optical absorption of
12 monolayer graphene amounts to 2.3 %, only.

13 The complete graphene/perovskite solar cell transmits 64.3 % of the incident light at 860 nm.
14 The transmitted light can be harvested in the bottom part of a tandem device. For this purpose,
15 the semi-transparent graphene/perovskite top cell is integrated into a four terminal tandem
16 design. This arrangement is particularly favourable, since it does not require current matching.
17 As an example we present the combination with an amorphous/crystalline silicon (a-Si:H/c-Si)²⁵
18 heterojunction solar cell as the bottom device. Other low band gap solar cells, e.g. organic or
19 chalcopyrite-based, may also be used for the bottom device.

20 Figure 5 shows the measured EQE, IQE and JV curves of the a-Si:H/c-Si solar cell measured as
21 single device (open circles) and as bottom solar cell with a graphene based perovskite top solar
22 cell as optical filter (full squares).



1
2 **Figure 5. a)** External and internal quantum efficiency spectra of the single a-Si:H/c-Si solar cell,
3 (open circles EQE, dashed line IQE), and EQE of the a-Si:H/c-Si bottom solar cell, measured
4 with graphene based perovskite solar cell as optical filter (full squares). b) Current density-
5 voltage characteristics of the single a-Si:H/c-Si solar cell, (open red circles), and the a-Si:H/c-Si
6 bottom solar cell under reduced light intensity calibrated to match J_{SC} as obtained from the EQE
7 measurement.

8
9 The single a-Si:H/c-Si solar cell shows a typical EQE and IQE with maxima of 93 % and 98 %, respectively. The integrated current amounts to 35.93 mA/cm^2 for this unoptimized device. Assuming an ideal high band gap top solar cell, the EQE of an a-Si:H/c-Si solar cell as bottom device is expected to vanish for $\lambda < 775 \text{ nm}$, while being unaffected for $\lambda > 775 \text{ nm}$. Using the graphene/perovskite solar cell as optical filter, the a-Si:H/c-Si solar cell EQE reduces to 60 % at 860 nm (full squares, Fig. 5). This correlates with the transmission of the graphene/perovskite solar cell with a maximum of 64.3 % at 860 nm. For $\lambda < 800 \text{ nm}$ the EQE follows the perovskite

1 solar cell transmission spectrum as plotted in Fig. 4. The integrated current of the a-Si:H/c-Si
 2 bottom cell is reduced by a factor of 2.5 to 14 mA/cm² compared to a single a-Si:H/c-Si
 3 heterojunction. The reduced light intensity further influences V_{OC} of the a-Si:H/c-Si solar cell in a
 4 logarithmic way as expected from diode characteristics.²⁶ Table 2 summarizes photovoltaic
 5 parameters of a-Si:H/c-Si solar cells as single (a) and bottom (b) solar cells. Due to the decrease
 6 in J_{SC} and V_{OC} the efficiency reduces from 18.5 % to 7.0 % with a graphene/perovskite solar cell
 7 as optical filter.

| Cell type | η (%) | V _{oc} (V) | J _{sc} (mA/cm ²) | FF (%) |
|------------------------|---------------|------------------------|--|-----------|
| (a) a-Si:H/c-Si single | 18.5 | 0.71 | 36.1 | 72.1 |
| (b) a-Si:H/c-Si bottom | 7.0 | 0.67 | 14.0 | 73.8 |
| (c) perovskite top | 6.2 | 0.90 | 12.6 | 55.0 |
| (d) projected tandem | 13.2 | | | |

8
 9 **Table 2.** Summarized solar cell parameters: (a) the a-Si:H/c-Si single solar cell, (b) the a-Si:H/c-
 10 Si solar cell as bottom solar cell in a 4-terminal tandem with a graphene based perovskite top cell
 11 as optical filter, (c) the graphene based perovskite top solar cell, and (d) the perovskite/a-Si:H/c-
 12 Si four terminal tandem efficiency .

13 As a proof of concept, the semi-transparent perovskite solar cell and the a-Si:H/c-Si solar cell are
 14 assembled into a tandem device. The efficiency of such a four terminal tandem solar cell
 15 amounts to 13.2 %. This is a relative increase of 30 % compared with the single perovskite solar
 16 cell with typical Au contacts (see Tab. 1 and Tab. 2). The efficiency of the presented tandem
 17 solar cell is comparable to recent results obtained with four terminal tandem designs using ITO
 18 electrodes⁹. It is important to note, that no anti-reflection (AR) coating was used for the
 19 perovskite top solar cell.

1 In summary, electrodes based on large area CVD-graphene combine a flexible transfer process
2 and unique optoelectronic properties. They therefore provide an excellent approach for the
3 realisation of perovskite/silicon tandem solar cells surpassing the Shockley-Queisser-limit for
4 single junction solar cells. We showed the successful implementation of a transparent large area,
5 high quality single layer graphene contact in perovskite solar cells. Electrical performance of
6 solar cells based on the layer sequence glass/SnO₂:F/TiO₂/CH₃NH₃PbI₃/spiro-
7 OMeTAD/graphene reached those of perovskite solar cells with standard Au contact. In detail,
8 identical open circuit voltages of around 1 V as well as identical charge collection efficiencies
9 proved defect free implementation of the monolayer graphene contact. Therefore, the presented
10 spiro-OMeTAD/graphene electrode can be used in four terminal and monolithic perovskite
11 tandem solar cells. A high series resistance can be reduced with the use of multiple graphene
12 layers.^{11,20} Graphene/perovskite solar cells showed a high optical transmission below the
13 perovskite band gap (64.3 % at 860 nm). These semi-transparent perovskite solar cells
14 ($\eta = 6.20\%$) were integrated in a four terminal tandem device with an a-Si:H/c-Si bottom solar
15 cell ($\eta = 7.0\%$). Power conversion efficiency of the tandem device was 13.2 %, thus increased
16 by 30% as compared to the respective perovskite single junction cell.

17

EXPERIMENTAL METHODS

Perovskite Solar Cell Preparation

Planar perovskite solar cells were prepared following the well-established layer sequence glass/FTO/TiO₂/CH₃NH₃PbI₃/spiro-OMeTAD. Therefore a ca. 40 nm thick compact TiO₂ layer was prepared by spray pyrolysis from titanium diisopropoxide bis(acetylacetonate) (Ti(acac)₂OiPr₂, Sigma Aldrich) at 460 °C on glass/SnO₂:F substrates (R = 8 Ω/sq, Solaronix). Prior to the deposition the substrates were cleaned with detergent/H₂O, acetone and isopropanol. After deposition they were fired at 450 °C for 30 min. A stoichiometric CH₃NH₃PbI₃ precursor solution containing 0.8 M of PbI₂ (Sigma Aldrich) and CH₃NH₃I (synthesized from CH₃NH₂ and HI⁶, Sigma Aldrich) in the mixed solvent γ -butyrolactone (GBL) and dimethyl sulfoxide (DMSO) with volume ratio 70/30 (v.%/v.%) was prepared under stirring at 60°C for 12 h. A 300 nm thick CH₃NH₃PbI₃ layer was spin coated at 1000 rpm for 10 s and 2000 rpm for 20 s. In the final spin coating stage 150 μ l toluene were dripped onto the sample, according to Ref.²⁷. The obtained CH₃NH₃PbI₃ layer was dried on a hotplate at 100 °C for 10 min. After cooling to room temperature the hole conductor 2,2',7,7'-tetrakis-(N,N-di-4-methoxy-phenyl-amino)-9,9'-spirobifluorene (spiro-OMeTAD, Merck) is applied by spin coating at 2000 rpm for 30 s, and left for 12 h in N₂ atmosphere. The spin coating formulation contained 80 mg spiro-OMeTAD dissolved in 1 ml chlorobenzene, 46.4 μ l of a bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, Lumtec) stock solution (170 mg/ml in acetonitrile), and 8.5 μ l of 4-tert-butylpyridine (Sigma Aldrich). Finally, gold electrodes were deposited by thermal evaporation at a base pressure of 10⁻⁷ mbar with a rate of 0.7 Å/s. The active area of perovskite solar cells was defined using a 0.16 cm² shadow mask. Since the perovskite film formation is sensitive to humidity all preparation steps were performed under N₂ atmosphere. An anti-reflection coating was omitted.

1 ***Graphene Electrode Preparation***

2 Large area CVD-graphene sheets were prepared via catalytic decomposition of methane on a
3 hot 25 μm thick copper foil ^{18,19}. Prior to the graphene deposition, the copper substrate was
4 polished and sonicated in acetone and isopropyl alcohol for 10 min. Residual surface oxides
5 were removed using acetic acid. The chemical vapour deposition of graphene is conducted in a
6 two-step process: First, the copper substrate is recrystallized in a hydrogen flow of 2 sccm at a
7 temperature of 1000°C. Subsequently, the hydrogen flow was reduced to 0.7 sccm and 11.4 sccm
8 of the carbon precursor methane was introduced. The latter growth step was carried out at a
9 pressure of 0.5 mbar for one hour. The final graphene sheets had a typical size of several square
10 centimeters. From these sheets smaller pieces of about 1 cm^2 were cut and used as transparent
11 electrodes. The graphene electrode was contacted using a Au grid finger, which was evaporated
12 onto spiro-OMeTAD. For optical and electrical characterization graphene sheets were transferred
13 onto a 300 nm SiO_2 layer on a c-Si wafer. According to Hall-effect measurements performed in
14 the van-der-Pauw geometry the graphene sheets are p-type showing a hole mobility of
15 1020 cm^2/Vs and a sheet resistance of 350 Ω/sq .

16 ***a-Si:H/c-Si Solar Cell Preparation & Characterisation***

17 Silicon heterojunction solar cells based on an n-type mono-crystalline silicon (c-Si) wafer and
18 thin hydrogenated amorphous silicon (a-Si:H) layers are used as bottom solar cell in a 4-terminal
19 tandem solar cell structure. The a-Si:H/c-Si solar cell preparation was performed according to
20 Ref. ²⁵. Intrinsic a-Si:H layers are used for passivation of the c-Si surface enabling open-circuit
21 voltages larger than 700 mV. The a-Si:H/c-Si solar cell had a V_{OC} of 709 mV and an J_{SC} of
22 35.93 mA/cm^2 .

1 *IV, EQE and UV-vis characterisation*

2 Current-voltage measurements of perovskite solar cells were performed using a “Steuernagel
3 Lichttechnik” sun simulator, mimicking AM 1.5G spectra. Solar cells with graphene and Au
4 reference electrodes were prepared and measured side by side on the same substrate. Cell size of
5 the a-Si:H/c-Si solar cell was 1 cm², while perovskite cell size was 0.16 cm² in case of the Au
6 reference electrode. CVD-graphene based electrodes had an area of 1.03 cm², including the Au
7 finger grid while being measured with an aperture of 0.16 cm² in size. All JV measurements
8 were performed in forward (from neg. to pos.) and reverse direction. A delay time of 40 ms with
9 20 ms acquisition time, corresponding to a scan speed of 0.167 V/s was chosen. According to
10 Refs ^{21,22} such a scan speed causes a clear appearance of the hysteresis effect, while slower and
11 faster measurements result in a smaller hysteresis of the JV curves. External quantum
12 efficiencies were measured on identically prepared samples without bias illumination. EQE of
13 the perovskite top solar cell was measured with a black absorber behind it. On the other hand
14 EQE of the bottom cell was measured with the perovskite solar cell as optical filter. IQE was
15 determined from reflection (R) and transmission (T) according to $IQE(\lambda) = \frac{EQE(\lambda)}{1-R(\lambda)-T(\lambda)}$. Diffuse
16 transmission and reflection was measured with a Perkin Elmer UV-vis spectrometer, equipped
17 with an integrating Ulbricht sphere and calibrated from an ISE certified white standard.

18
19 AUTHOR INFORMATION

20 **Corresponding Author**

21 Felix Lang, e-mail felix.lang@helmholtz-berlin.de, Phone: +00 49 30 8062 41354, Fax +49 30
22 8062-41333

1 **Author Contributions**

2 The manuscript was written through contributions of all authors. All authors have given approval
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12 J. Kegel, E. Conrad, and M. Mews.

13 **Supporting Information Available:** Current density-voltage characteristics of perovskite solar
14 cells in forward and reverse direction for Au and graphene electrodes respectively. This material
15 is available free of charge via the Internet. <http://pubs.acs.org>

16

17 **ABBREVIATIONS**

18 silver nanowire, AgNW; poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, PEDOT:PSS;
19 carbon nanotube networks, CNT; chlorobenzene, CBZ; γ -butyrolactone, GBL; dimethyl
20 sulfoxide, DMSO; crystalline silicon, c-Si; anti-reflection, AR; titanium diisopropoxide
21 bis(acetylacetonate), Ti(acac)₂OiPr₂; open circuit voltage, V_{OC}; fill factor, FF; short circuit
22 current, J_{sc}; current-voltage, IV; transmission, T; transparent conductive oxide, TCO; indium tin

1 oxide, ITO; fluorine doped tin oxide, SnO₂:F; hole transport material, HTM; external quantum
2 efficiency, EQE; internal quantum efficiency, IQE; chemical vapour deposition, CVD; 2,2',7,7'-
3 Tetrakis-(N,N-di-4-methoxy-phenyl-amino)-9,9'-spirobifluorene, spiro-OMeTAD

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