

## Supporting Information

**Contactless and spatially-resolved determination of current-voltage curves in perovskite solar cells via photoluminescence**

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**1. Preparation of perovskite films**

## Step 1: Substrate cleaning

In brief, Fluorine doped tin oxide (FTO)/glass substrates were consecutively rinsed with soap, acetone, 2-propanol, ethanol, and deionized (DI) water in an ultrasonic bath. After that, the substrates were UV-ozone pre-treated for 15 minutes before being immediately transferred to a N<sub>2</sub> purging glove box.

## Step 2: Perovskite film preparation

Depending on specific requirements, different types of samples were prepared as follows:

In order to study the effect of passivation layers, double cation Cs<sub>0.15</sub>FA<sub>0.85</sub>PbI<sub>2.55</sub>Br<sub>0.45</sub> perovskite films were employed. The precursor solution was prepared by mixing 1.2 M PbI<sub>2</sub>, 1.1 M formamidinium iodide (FAI), 0.2 M lead bromide (PbBr<sub>2</sub>), and 0.2 M cesium bromide (CsBr) in 1 mL anhydrous N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (8:2, v/v) (DMF: DMSO solution). The perovskite deposition process was done by employing a two-step spin coating program: first the substrate was rotated at 1000 rpm for 10 s with an acceleration rate of 100 rpm/s, after that at 4000 rpm for 25 s with an acceleration rate of 1000

rpm/s. Approximately 150  $\mu$ L of chlorobenzene was drained to the spinning substrate 8 s prior to the end of the spinning program at the second step. After that, all substrates were annealed on a hot plate at 100°C for 45 minutes. One bare film was kept for comparisons, and another one was coated with 2D perovskite passivation layers with a thickness of approximately 20 nm.<sup>[1]</sup>

In order to study the effect of bandgap on the film performance, 3 different film compositions were prepared as follows:

- For the 1.52 eV bandgap perovskite  $\text{FAPbI}_3$ , 1.3M of FAI and 1.3M of  $\text{PbI}_2$  were mixed well in 1 ml DMF:DMSO solution.
- For the 1.62 eV bandgap perovskite  $\text{Rb}_{0.03}\text{Cs}_{0.07}\text{MA}_{0.138}\text{FA}_{0.762}\text{PbI}_{2.55}\text{Br}_{0.45}$ , 1.1M FAI, 1.2M  $\text{PbI}_2$ , 0.2M MABr, and 0.2M  $\text{PbBr}_2$  were mixed in 1 ml DMF:DMSO(4:1 volume ratio) solution. 70  $\mu$ l of CsI solution (1.3M in DMSO) and 30  $\mu$ l of RbI solution (1.3M in DMSO) were added into the base precursor.
- For the 1.72 eV bandgap perovskite  $\text{Rb}_{0.05}\text{Cs}_{0.1}\text{MA}_{0.15}\text{FA}_{0.75}\text{PbI}_2\text{Br}$ , 0.75 ml of  $\text{FAPbI}_2\text{Br}$  (1.3M in DMF/DMSO 4:1 volume ratio), 0.15 ml  $\text{MAPbI}_2\text{Br}$  (1.3M) in 1 ml DMF:DMSO solution), 0.1 ml  $\text{CsPbI}_2\text{Br}$  (1.3 M in DMSO) and 0.05 ml RbI (1.3 M in DMSO) were mixed well.

All samples were deposited by the spin coating and annealing procedures mentioned above.

## 2. Fabrication of perovskite solar cells (PSCs)

The fabrication process of perovskite solar cells was described in detail in our previous work.

<sup>[2]</sup>FTO/glass substrates were cleaned and then treated in a UV-ozone machine for 15 minutes.

Subsequently, a ~70 nm layer of compact  $\text{TiO}_2$  (cp- $\text{TiO}_2$ ) layer and a ~80 nm layer of mesoporous (mp- $\text{TiO}_2$ ) were deposited on the substrates sequentially according to the processes described in Ref [2]. A thin (~3 nm) poly(methyl methacrylate): phenyl-C60-

butyric acid methyl ester (PMMA:PCBM) passivation layer was deposited on the electron transport layers (ETLs) coated substrate at a spin rate of 4000 rpm for 15 s with an acceleration of 4000 rpm/s. Details regarding the preparation of PMMA:PCBM passivation solution can be found in our previous work.<sup>[3]</sup> This was followed by an annealing step of 10 minutes on a hotplate at 100 °C. Quadruple cation perovskite ( $\text{Cs}_{0.07}\text{Rb}_{0.03}\text{FA}_{0.765}\text{MA}_{0.135}\text{PbI}_{2.55}\text{Br}_{0.45}$ ) perovskite precursor was prepared by dissolving a mixture of 1.1 M formamidinium iodide (FAI), 0.2 M methyl ammonium bromide (MABr), 1.2 M lead iodine ( $\text{PbI}_2$ ) and 0.2 M lead bromide ( $\text{PbBr}_2$ ) in 1 ml DMF:DMSO (in 4:1 volume ratio) solution. The perovskite deposition process was done by two-steps spin-coating programs, which was similar with the one mentioned above. Subsequently, the samples were tempered at 100 °C for 30 minutes and then, the substrates were cooled down. During the cooling down process, n-butylammonium iodide (n-BAI) solution in 2-propanol (1 mg/ml) was spin-coated on the substrates using a spin speed of 5000 rpm for 15 s with an acceleration of 5000 rpm/s for the 2D perovskite film formation. The substrates were then annealed on a hotplate for 10 minutes at 100 °C temperature. For hole transport layers (HTLs), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) solution was prepared by dissolving 73.5 mg Spiro-OMeTAD in 1 ml chlorobenzene, and the solution was doped with 17.5  $\mu\text{L}$  of bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) (520 mg/mL in acetonitrile) and 28.5  $\mu\text{L}$  of 4-tertbutylpyridine (4-TBP) to enhance the p-type conductivity. The Spiro-OMeTAD layer was spin-coated at 3500 rpm for 30 s with a ramp rate of 3500 rpm/s. The coated substrates were dried overnight in a humidity-controlled box to ensure proper oxidation of the Spiro-OMeTAD film. On the following day, ~80 nm gold layer was deposited on the coated substrates in a thermal evaporation process inside a  $\text{N}_2$  filled glovebox. The active area of the cell (0.165  $\text{cm}^2$ ) was defined using a shadow mask during the evaporation process.

### 3. Silicon solar cell fabrication and characterization

A high-quality crystalline silicon (c-Si) solar cell was fabricated, as detailed in our previous work.<sup>[4]</sup> It had a full-area phosphorus-doped polysilicon contact layer on the rear side and a standard boron diffusion layer on the front side. The solar cell size was 2 cm × 2 cm.

The current density–voltage (JV) characteristic and Suns- $V_{oc}$  measurements of the cell were measured in-house by utilizing a Sinton Instruments FCT-450 tool at room temperature. The solar cell achieves an efficiency of 22.78%, with a  $V_{oc}$  of 0.683 V, a  $J_{sc}$  of 41.64 mA cm<sup>-2</sup>, and an FF of 80.1% using our in-house solar simulator.

### 4. Fabrication of the double-side coated AlO<sub>x</sub>/Si/AlO<sub>x</sub> wafer

A phosphorus-doped n-type c-Si wafer with a thickness of 275 μm (Semiconductor wafer Inc) was immersed in a tetramethylammonium hydroxide (TMAH) solution to remove saw damage and then cleaned by an RCA process. The wafer was passivated both sides by a 20-nm layer of AlO<sub>x</sub> by an atomic layer deposition (ALD) technique. After that, the sample was annealed in a forming gas consisting of H<sub>2</sub>(5%) and N<sub>2</sub> (95%) at 400 °C for 30 minutes to activate the passivation. The Suns- $V_{oc}$  measurement on the passivated wafer was performed using a quasi-steady-state photoconductance (QSSPC) method and a Sinton Instruments WCT-120 tool at room temperature. The minority carrier lifetime of the passivated wafer is 1.78 ms at an injection level of 10<sup>15</sup> cm<sup>-3</sup> and the saturation current density is 8.6 fA/cm<sup>2</sup>.

### 5. Determination of absorptivity

Global absorptivity of each sample was acquired using a PerkinElmer 1050 spectrophotometer equipped with an integrating sphere detector. Absorptivity  $A(E)$  was calculated from reflectivity ( $R(E)$ ) and transmissivity ( $T(E)$ ) measurements for the double-side coated AlO<sub>x</sub>/Si wafer and perovskite films ( $A(E) = 1 - R(E) - T(E)$ ). For completed devices, i.e. the Si and perovskite solar cells, since the rear side of the cells were fully covered

by metals, the cell absorptivity is simply  $A(E) = 1 - R(E)$ . All measurements were performed with a wavelength ranging from 300 to 1200 nm, beyond which our imaging tools were insensitive.

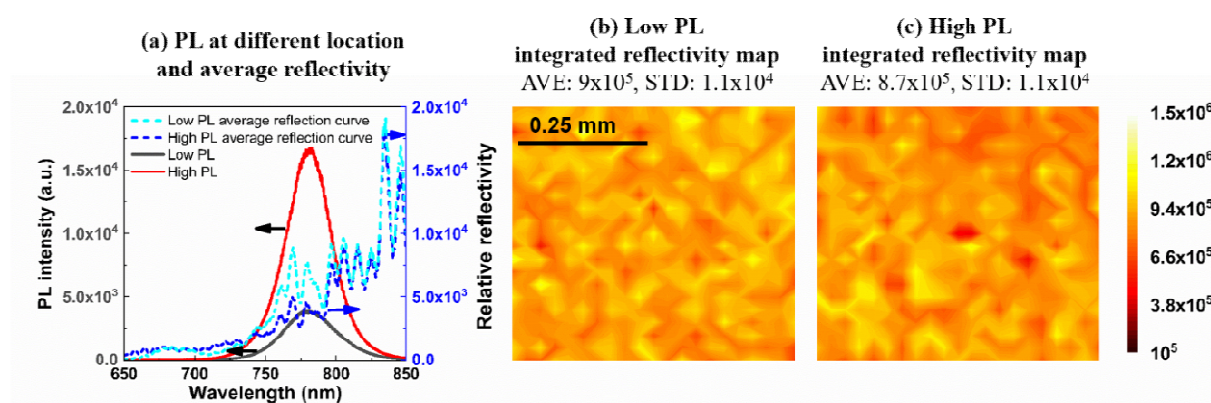
Local reflectivity map of PSCs was measured by using  $\mu$ -PL/Raman system with a broad band radiation from a supercontinuum NKT laser whose tunable wavelength range is 480–2000 nm.

## **6. Suns-photoluminescence measurements**

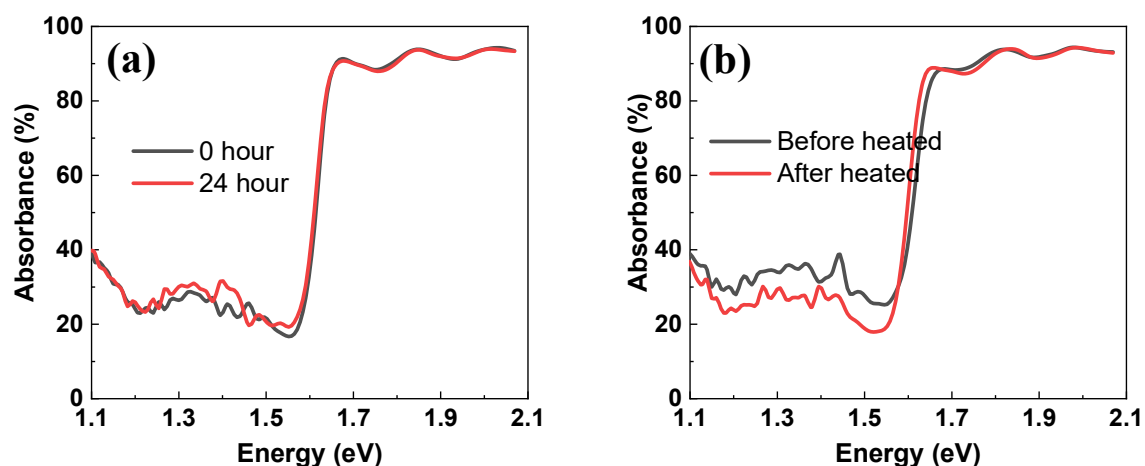
Two separate photoluminescence (PL) imaging systems were employed in this work. They were both equipped with Si charge-coupled device (CCD) array detectors. For Si wafers and solar cells, the laser excitation wavelength was 808 nm and the intensity was determined by a calibrated Si solar cell. For perovskite films and solar cells, the light-emitting diode (LED) excitation wavelength was 430 nm and the intensity was calibrated using a high-quality working perovskite solar cell. During the measurement process, after changing the illumination intensity, the perovskite samples were kept there for 15 seconds in order to get the steady-state condition before taking the measurements.

## **7. Determination of scaling factor (SF) for PSCs**

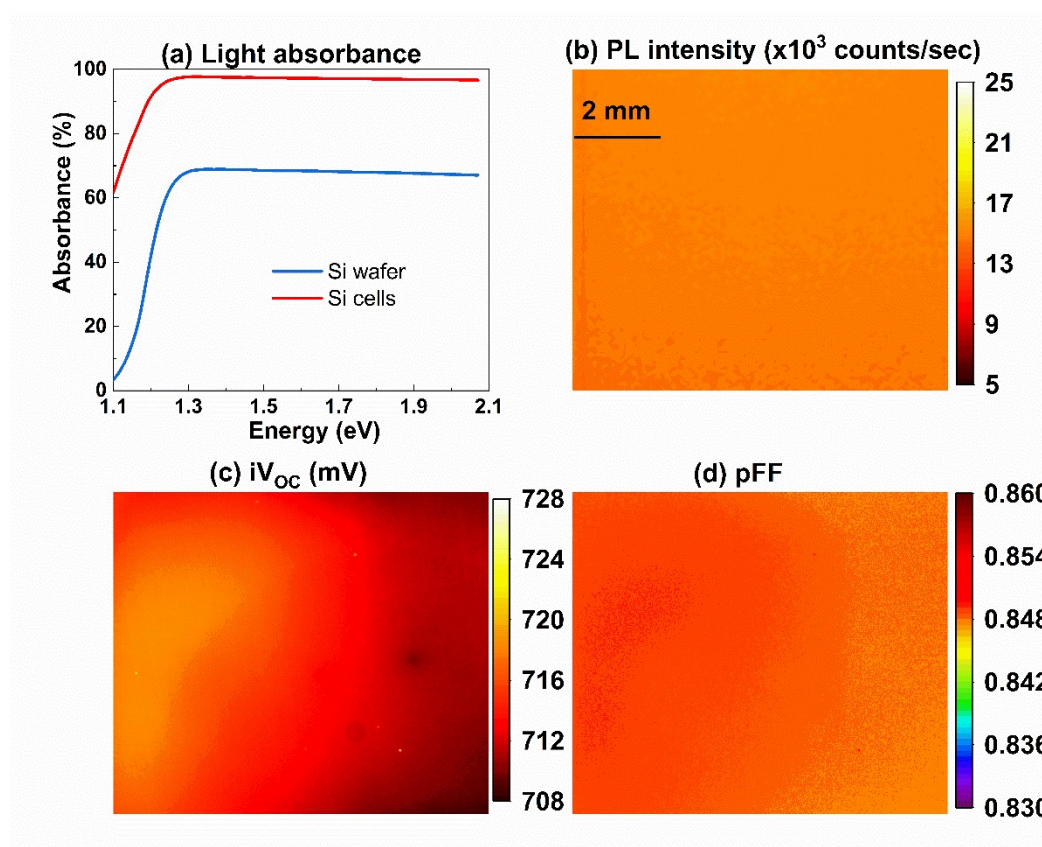
Unlike Si, the QSSPC method cannot be applied to determine the implied open circuit voltage of perovskite cells and films. Therefore, we used a well working PSC ( $V_{oc} > 1.1V$ , PCE > 20%) and measured its open-circuit voltage at the fresh stage under 1 Sun. We assumed that, at the fresh stage, the cell's transport layers and interfaces were good enough to transfer all electrons and holes to the electrodes, i.e. the real  $V_{oc}$  approached the  $iV_{oc}$ . Therefore this real  $V_{oc}$  could be used to determine the SF value. In addition, this SF value should be independent of the illumination intensity and cell quality, thus it could be applied across different perovskite samples.



**Figure S1:** (a) PL (left) and relative reflectivity (right) spectra at different regions of a PSC. Integrated relative reflectivity maps of the PSC at (b) low and (c) high PL intensity regions. The relative reflectivity spectra were obtained by measuring a white light source reflected from the sample to the detector of a micro-PL mapping system, from 650 to 850 nm around the PL spectra of the PSC.

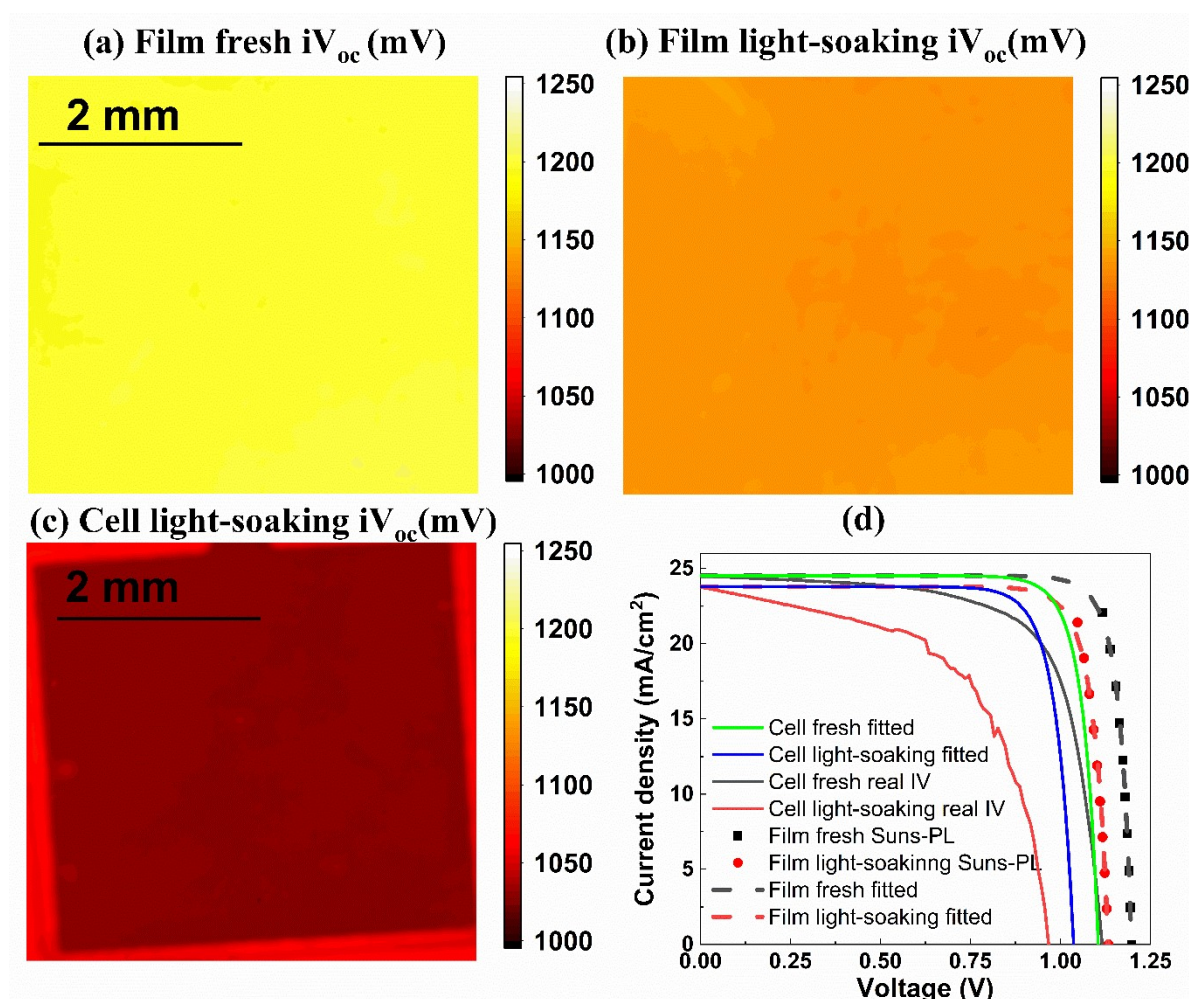


**Figure S2:** Global absorptivity spectra of a PSC before and after (a) air exposure for 24 hours and (b) being annealed at 90 °C for 30 minutes.



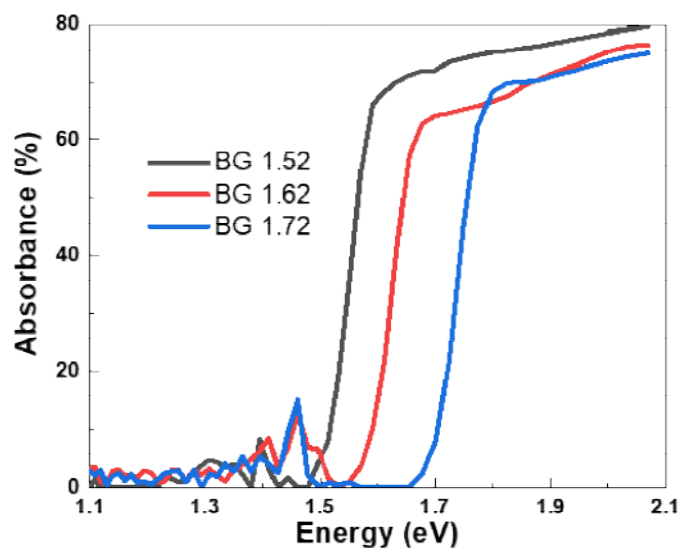
**Figure S3:** (a) Global absorptivity of the double-side coated  $\text{AlO}_x/\text{Si}/\text{AlO}_x$  wafer and Si solar cell. (b-d) PL intensity,  $iV_{oc}$ , and pseudo-FF images, respectively, of the double-side coated  $\text{AlO}_x/\text{Si}/\text{AlO}_x$  wafer obtained from the Suns-PL imaging method.





**Figure S4:**  $iV_{oc}$  images of (a) a bare perovskite film at a fresh stage and (b) after light soaking, and (c) a finished PSC after light soaking (its fresh stage image was presented in **Figure 3c** in the main text). (d) Real and pseudo JV curves of the cell and film before and after the light soaking test.





**Figure S5:** Absorptivity spectra of different perovskite films with different bandgaps investigated in Figure 7 in the main text.

**Table S1:** Means and standard deviations of  $iV_{oc}$  of the PSC before and after being heated at 90°C in 30 minutes.

$iV_{oc}$ (mV) Sun	As-prepared		Heated	
	AVE	STD	AVE	STD
1	1095.3	6.8	1056.4	12.7
0.9	1091.7	7.3	1051.2	12.3
0.8	1086.6	7.5	1046.9	11.8
0.7	1079.5	7.4	1042.2	11.2
0.6	1070.9	7.2	1037.2	10.4
0.5	1060.1	7.1	1023.9	12.0
0.4	1050.7	6.9	1015.3	11.1
0.3	1041.6	6.0	1004.8	9.6
0.2	1020.2	6.1	991.0	7.4
0.1	977.0	7.4	972.7	3.3
0.05	962.7	2.1	962.1	0.7

**Table S2:** Means and standard deviations of  $iV_{oc}$  of the PSC before and after the light-soaking test at 1 Sun (without temperature control) in 30 minutes.

$iV_{oc}$ (mV) Sun	<b>As-prepared</b>		<b>Light-soaking</b>	
	AVE	STD	AVE	STD
1	1107.0	2.9	1035.1	10.4
0.9	1101.6	3.4	1030.3	10.4
0.8	1096.0	3.7	1024.7	10.6
0.7	1090.8	3.9	1019.3	10.4
0.6	1083.9	4.0	1012.5	10.3
0.5	1075.5	4.0	1004.5	10.2
0.4	1063.6	3.9	996.9	9.2
0.3	1048.8	3.7	983.6	8.9
0.2	1019.9	6.2	970.2	6.6
0.1	976.2	7.9	954.5	2.4
0.05	962.8	1.9	946.1	0.5

**Table S3:** Means and standard deviations of  $iV_{oc}$  of the PSC during the air stability test.

$iV_{oc}$ (mV) Sun	<b>0h</b>		<b>1h</b>		<b>24h</b>	
	AVE	STD	AVE	STD	AVE	STD
1	1123.0	15.0	1109.6	18.0	1067.8	15.2
0.9	1118.8	15.2	1103.1	17.7	1063.6	15.0
0.8	1114.7	15.1	1097.6	17.1	1059.2	14.7
0.7	1108.5	15.4	1092.9	16.8	1054.4	14.3
0.6	1104.0	14.8	1087.3	16.3	1048.9	13.7
0.5	1095.9	14.9	1083.6	16.0	1042.6	12.9
0.4	1087.9	14.4	1069.3	18.0	1028.1	14.3
0.3	1077.8	13.2	1057.5	17.1	1016.5	13.2
0.2	1053.9	14.9	1041.4	15.1	1001.1	11.1
0.1	1028.7	10.7	1018.7	9.3	979.3	6.2
0.05	1009.0	3.8	1006.6	2.4	966.5	1.1

## References

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