

Supporting information

Perovskite production

The substrates were of similar thickness and size (after cutting the wafers with a use of diamond knife), differing by the doping type and resistivity. The wafer resistivity and thickness provided by the producer (Sil'tronix Silicon Technologies) are given in Table S1. Wafers have been firstly cut into smaller pieces (max. $2 \times 2 \text{ cm}^2$), then cleaned in acetone at room temperature for 15 min, then cleaned in isopropanol at room temperature for 15 min, then abundantly rinsed with deionised water and dried with air blow. The native silicon oxide (SiO_x) was not etched, and its thickness has been estimated using spectroscopic ellipsometry to be around 2 nm. Next, the silicon substrates were placed in UV/ O_3 chamber for 30 min to increase their hydrophilicity which is necessary for successful perovskite deposition. After the UV- O_3 cleaning process, silicon substrates were immediately placed in the Jacomex glovebox, where perovskite deposition has been performed within 45 min from taking them from UV/ O_3 chamber (including 15 min transit in a vacuum chamber of the glovebox and approximately 30 min of perovskite deposition on usually 16 substrates). It has been observed, that when producing more samples (longer total time of perovskite deposition), the UV/ O_3 effect is not maintained, and perovskite deposition becomes more challenging, resulting in uneven coverage and every time increasing regions without perovskite film at all. Bare silicon substrates that were measured by KPFM were treated together with substrates used for perovskite deposition and no additional treatment was done before KPFM measurements.

Table S1 The parameters of the c-Si substrates used in the experiments

Parameter / Sample	p-Si	n-Si
Resistivity min ($\Omega \text{ cm}$)	1-10	1-10
Dopant	B	P
Doping concentration (cm^{-3})	$1.5 \times 10^{16} - 1.4 \times 10^{15}$	$4.9 \times 10^{15} - 4.5 \times 10^{14}$
Thickness (μm)	250	250
Orientation	(100)	(100)
Growth method	Czochralski	Czochralski

Perovskite solution is prepared from the recipe: 22.39 mg MABr (Greatcell Solar Materials), 73.40 mg PbBr₂ (Alfa Aesar), 171.97 mg FAI (Greatcell Solar Materials) and 507.11 mg PbI₂ (Alfa Aesar), dissolved in 800 μ l DMF (Sigma Aldrich) and 200 μ l DMSO (Sigma Aldrich). The recipe includes PbI₂ excess, which has shown to improve perovskite efficiency. The solution is then left on a magnetic stirrer for at least 3 hours. Around 15 min before perovskite deposition, 42 μ l CsI stock solution (194.86 mg CsI (Aldrich) dissolved in 500 μ l DMSO) is added. Humidity level inside the glovebox does not exceed 30 ppm and O₂ quantity does not exceed 10 ppm. Ten seconds before the end of the spinning program, antisolvent chlorobenzene (Sigma Aldrich) is deposited. After deposition, samples are immediately placed on a hot plate to anneal for 30 min in 100 °C in N₂ atmosphere. The trends of the characterisation results presented in this work has been reproduced in 3 different batches.

Perovskite film characterisation

SEM

The SEM images were acquired using Zeiss Merlin scanning electron microscope.

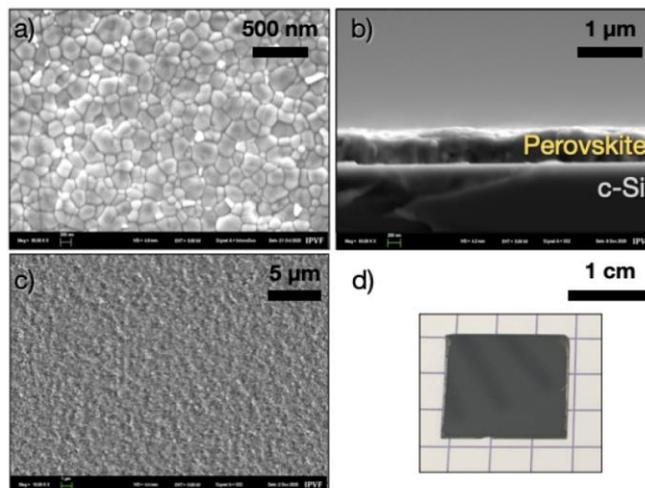


Figure S1 SEM images of the perovskite surface (a and c), cross-section (b) and photo of the PVK/c-Si sample (d)

XRD

The measurements were done in clean-room ambient conditions, using the Panalytical XRD Empyrean X-ray diffractometer in Bragg-Brentano configuration. The X-ray source was Cu $K\alpha_{1,2}$ radiation, $\lambda = 1.5418 \text{ \AA}$.

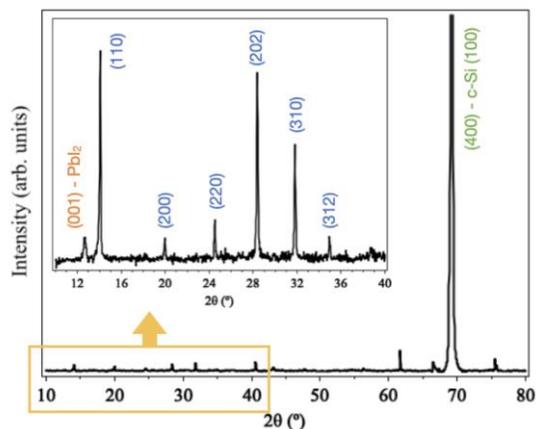


Figure S2 XRD pattern of the PVK/c-Si samples with assigned peaks

UPS

UPS measurements for the study of the work function and valence band position with respect to Fermi level have been performed using the same system, operating at a base pressure of 10^{-6} Pa, using a He-gas discharge lamp (He I $h\nu = 21.2 \text{ eV}$). UPS spectra were conducted with a step size of 0.01 eV , pass energy 2.95 eV and dwell time 20 ms , and with a take-off angle of 90° . The bias applied to the sample was between $8\text{-}9 \text{ V}$. The electron binding energy scale was calibrated using the Fermi edge of gold substrates cleaned with argon ion bombardment (2 kV). UPS spectra were numerically corrected for satellite peaks that arise from the polychromatic He I radiation (with He I α emission line occurring at 21.22 eV with relative intensity being 100% , the satellites are He β with emission line at 23.09 eV and relative intensity of around 1.5% and He γ with emission line at 23.74 eV and relative intensity 0.5%). Work function was determined using the intersection between the baseline and a linear fit to the main feature. EVBM was calculated using recommended for perovskite materials semi-log extrapolation of the main feature in the valence band region to the background signal. Spectra taken with UPS are typically assigned an uncertainty less than 0.12 eV .

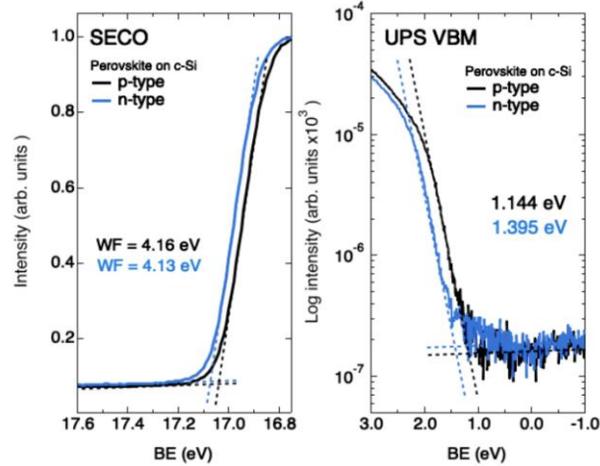


Figure S3 UPS results showing the secondary electron cut-off (a) determining the work function (WF) of the perovskite on p-Si (black lines) and n-Si (blue lines), and the Fermi edge (b) showing the determination of the valence band to Fermi level distance (VBM). For both samples, the VBM value indicates rather n-type character of the PVK surface.

Drift-diffusion simulations

Drift-diffusion simulations have been performed to support the discussion of the results. Regarding the generation and recombination processes in silicon it includes the optical generation, radiative and non-radiative recombination. The Shockley-Read-Hall recombination is implemented for the surface trap defects as well as in the bulk. The simulated structure is 250 μm thick c-Si (with dopants acceptors or donors, with the density of 10^{15} cm^{-3} and $5 \times 10^{15} \text{ cm}^{-3}$, respectively, depending on the silicon doping type) and with 1 nm surface layer to include surface traps. The surface traps have the density of $1.5 \times 10^{11} \text{ cm}^{-2}$. The defects are located in the midgap $\pm 0.05 \text{ eV}$ (electron donor traps are located 0.05 eV below the midgap, and the electron acceptor traps are located 0.05 eV above the midgap). Before reaching the equilibrium with the semiconductor, all the electron trap states above the intrinsic Fermi level are empty and the states below – filled. This structure has been simulated in the equilibrium conditions (in the dark) and under 980 nm laser illumination.

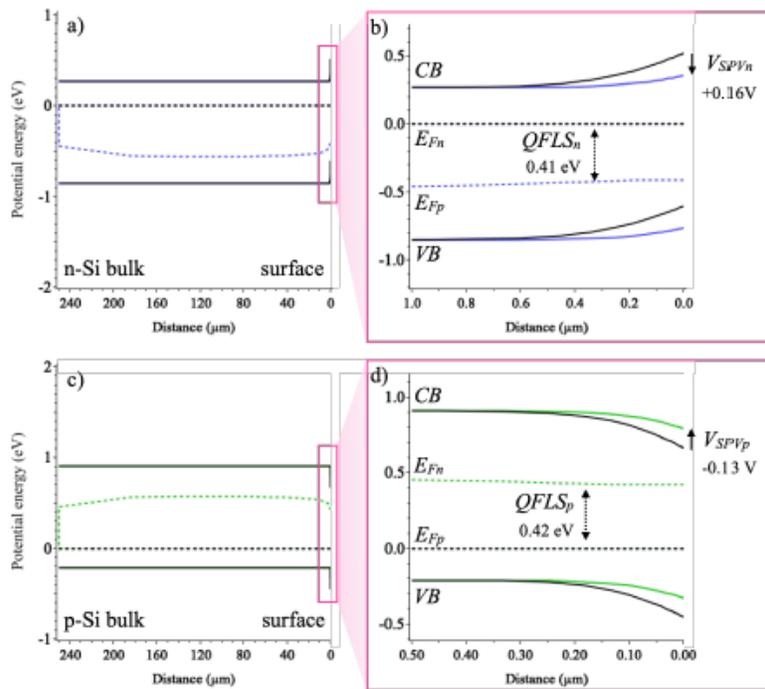


Figure S4 Simulations of the SPV of bare silicon under 980 nm for n-Si (a and b) and p-Si (c and d).

Similar drift-diffusion simulations as for bare c-Si samples have been performed in case of perovskite on silicon samples. The model used for this purpose has been mentioned elsewhere [S1]. The model is quite simple, but if we assume only electronic processes occurring in c-Si under 980 nm illumination, we can obtain quite well reproduction of the results, which can help for the explanation of the origins of the observed SPV. The simulation results are shown below.

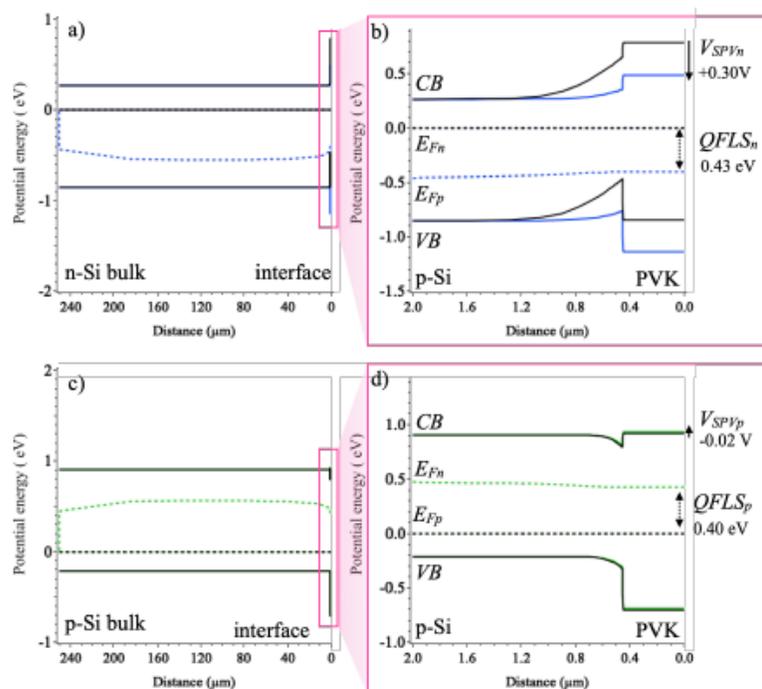


Figure S5 Simulations of the SPV of the Si/PVK samples under 980 nm illumination. We observe only the interface component of SPV and the light absorption takes place only in silicon. The interface band alignment between n-Si and PVK (b) is upward and results in positive SPV. Almost negligible downward band bending at the interface between p-Si and PVK results in very small negative SPV, as measured by KPFM.

Simulations of the SPV under 785 nm and 980 nm are more challenging as they need to include ionic contribution to the SPV, and they were beyond this study.

SPV measurements – experimental details

KPFM

KPFM measurements were performed using a HORIBA/AIST-NT (TRIOS platform) scanning probe microscopy system. Scans were performed using conductive Pt/Ir AFM tip in amplitude modulation mode, using the two-pass mode. In the first pass sample topography is scanned in a non-contact mode (at the distance $\sim 1-5$ nm from the sample surface). The probe is then lifted by 30 nm to follow the measured topography registering *CPD* variation over the same area. The measuring direction of $2 \times 2 \mu\text{m}^2$ scans was

from the bottom left corner to the top. For laser-based cantilever deflection detection, a 1310 nm photodiode was used, providing no unwanted band-to-band light-excitation of any of the sample components (c-Si substrate and perovskite thin film). The system thus provides surface potential measurements in the dark. The TRIOS platform (Transmission and Reflection Input/Output System) combines an atomic force microscope, capable of performing electrical measurements, like KPFM, with external illumination sources, enabling measurements in the presence or absence of light.

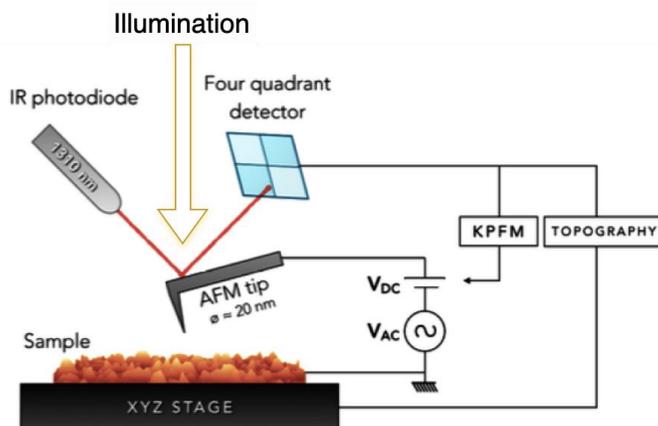


Figure S6 KPFM setup

The table of laser (Table S2) includes nominal power set on the laser source (mW), the diameter of the beam spot (μm), the power measured on the sample after passing through optical system (μW).

Table S2 Parameters of the lasers used in KPFM experiments

Wavelength (nm)	Energy (eV)	Nominal power (mW)	Power measured on the sample (μW)	Spot size diameter (μm)	Power density (W/m^2)
980	1.27	2	51	205	1545
785	1.58	3	68	240	1511
488	2.54	4	62	230	1486

All measurements were done in ambient conditions. The sensitivity of *CPD* measurements using above mentioned conditions is ± 20 mV. All the samples were kept in the dark to stabilise for around 45 min prior to dark measurements. The samples were grounded on the Si side using silver paste.

As mentioned, *CPD* value can give us the surface work function of the sample, when the work function of the tip is known. For this purpose, highly oriented pyrolytic graphite crystal (HOPG) is used to determine the work function of the tip. This material is often used as a reference surface with known WF, because of its availability and low cost, among the others. HOPG crystal can be easily exfoliated, exposing fresh surface to measure its work function. WF of HOPG surface under air condition is 4.60 eV [S2, S3]. During experiments, tip calibration was performed before and after measurements of each sample, also to assure no change of the tip work function due to possible halide migration to the tip [S4].

MIS

The experimental set-up for SPS in MIS operation mode used in this work is schematically presented in the Figure S5 (with the exception that the sample was not in the cryostat). It includes a 250 W halogen tungsten lamp along with a 0.22m SPEX grating monochromator, a filter to cut off the high-order diffraction and a PTI OC4000 optical chopper.

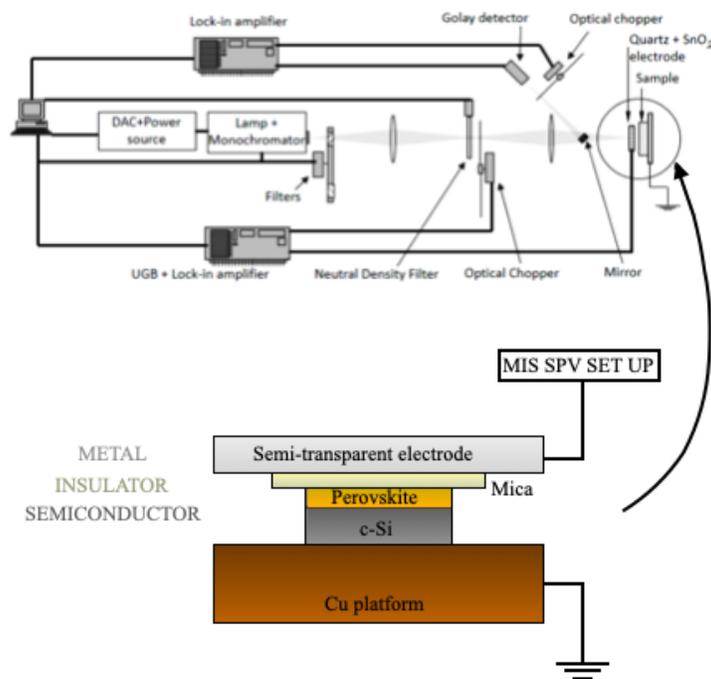


Figure S7 MIS setup[S5-S6]

The scan was from long towards short wavelengths. The photon flux was kept constant at its value at 500 nm or 600 nm. This is realized by means of a spectrally flat Golay detector and a neutral density filter driven by its signal. A monochromator with 1200gr/mm grating was used. With 1.25 mm slits the spectral resolution is 5 nm, while with 2.5 mm slits it is 10 nm. The photon flux in both cases was kept constant at about the same value $\Phi = 6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, since for 1.25 mm slit it was measured at 600 nm, while for 2.5 mm slits - at 500 nm. Below 500 nm the light intensity rapidly decreases, and it is almost impossible to keep the photon flux constant. In the measurements the semi-transparent electrode gently touched the sample, which was positioned on a Cu platform. The insulator used was a mica sheet ($\sim 15 \mu\text{m}$) placed between the electrode and the sample.

References SI

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