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Surface photovoltage study of metal halide perovskites deposited directly on crystalline silicon

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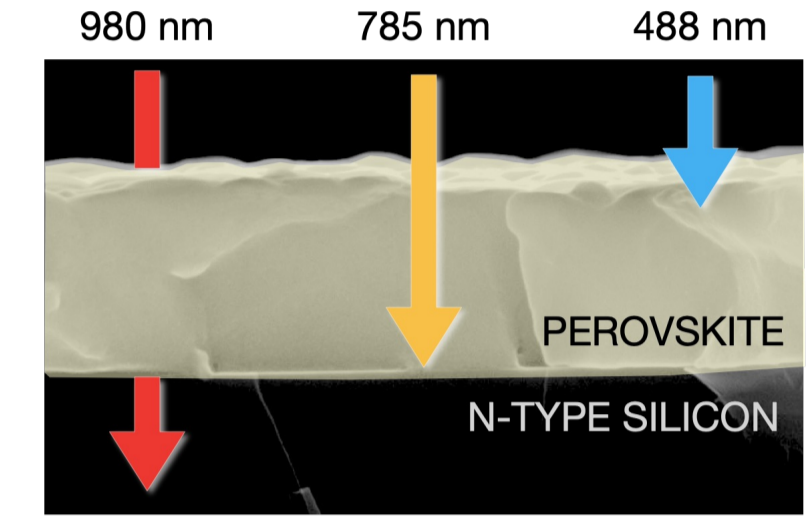
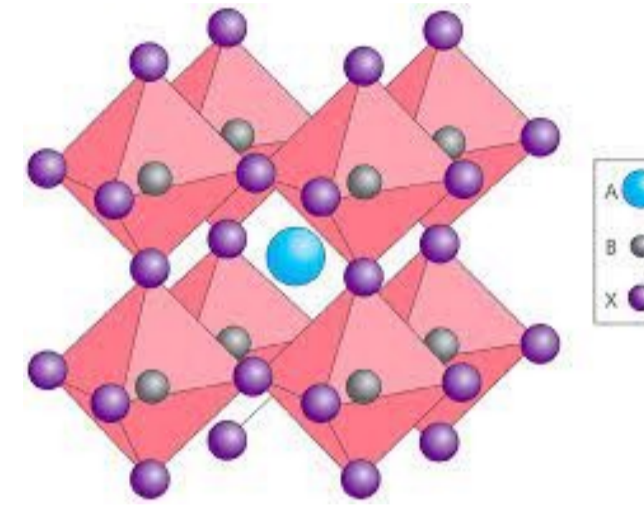
Motivation:

- Perovskite-silicon tandem solar cells are a prospective system for overcoming the single-cell efficiency limit [1].
- This is due to the matured Si technology combined with the tunable bandgap around 1.6 eV via compositional engineering, high absorption coefficient and steep absorption edge of the perovskite (PVK) materials.
- Most of the research considers 2-Terminal and 4-Terminal PVK/Si tandems, where these two materials are NOT in direct contact.
- First photovoltaic device based on **direct heterojunction** between PVK and n-Si proposed in [2].
- Further research is needed to fully understand and exploit the PVK/Si system with direct contact between the two materials.

A challenge: Understand the carrier generation, transport and recombination in the PVK and at the PVK/Si interface and surface.

Experimental samples: ABX₃ perovskites on c-Si

- Triple cation mixed halide PVK thin films Cs_{0.05}(MA_{0.14},FA_{0.86})_{0.95}Pb(I_{0.84},Br_{0.16})₃ [MA is methylammonium, CH₃NH₃, and FA is formamidinium, CH₂(NH₂)₂];
- Deposited via spin-coating directly on n-type crystalline Si substrates (details in [3]);
- SEM → high-quality surface of the PVK layers, thickness of 400-500 nm;
- XRD → highly crystalline nature of the PVK films with only minor PbI₂ phase;
- PL → bandgap of 1.63 eV.

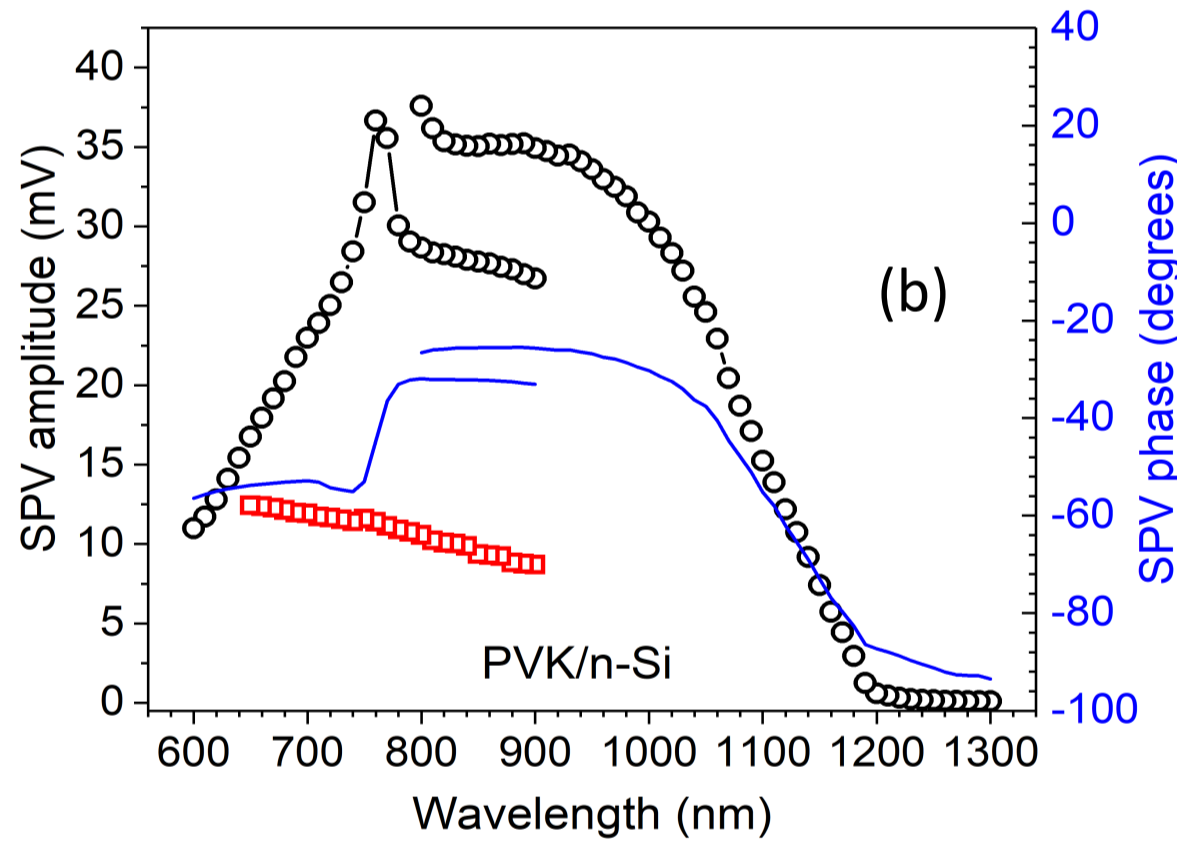
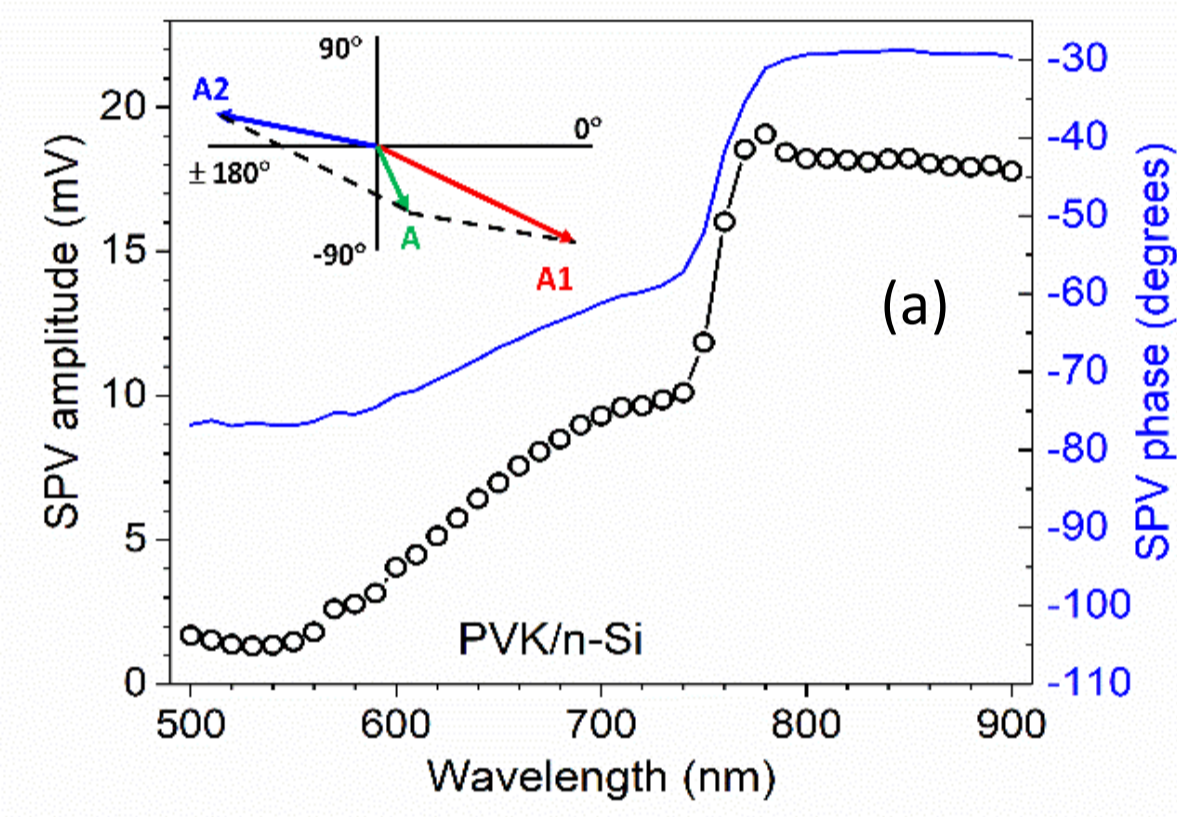


Surface Photovoltage (SPV) methods: metal-insulator-semiconductor (MIS) and Kelvin probe force microscopy (KPFM) modes

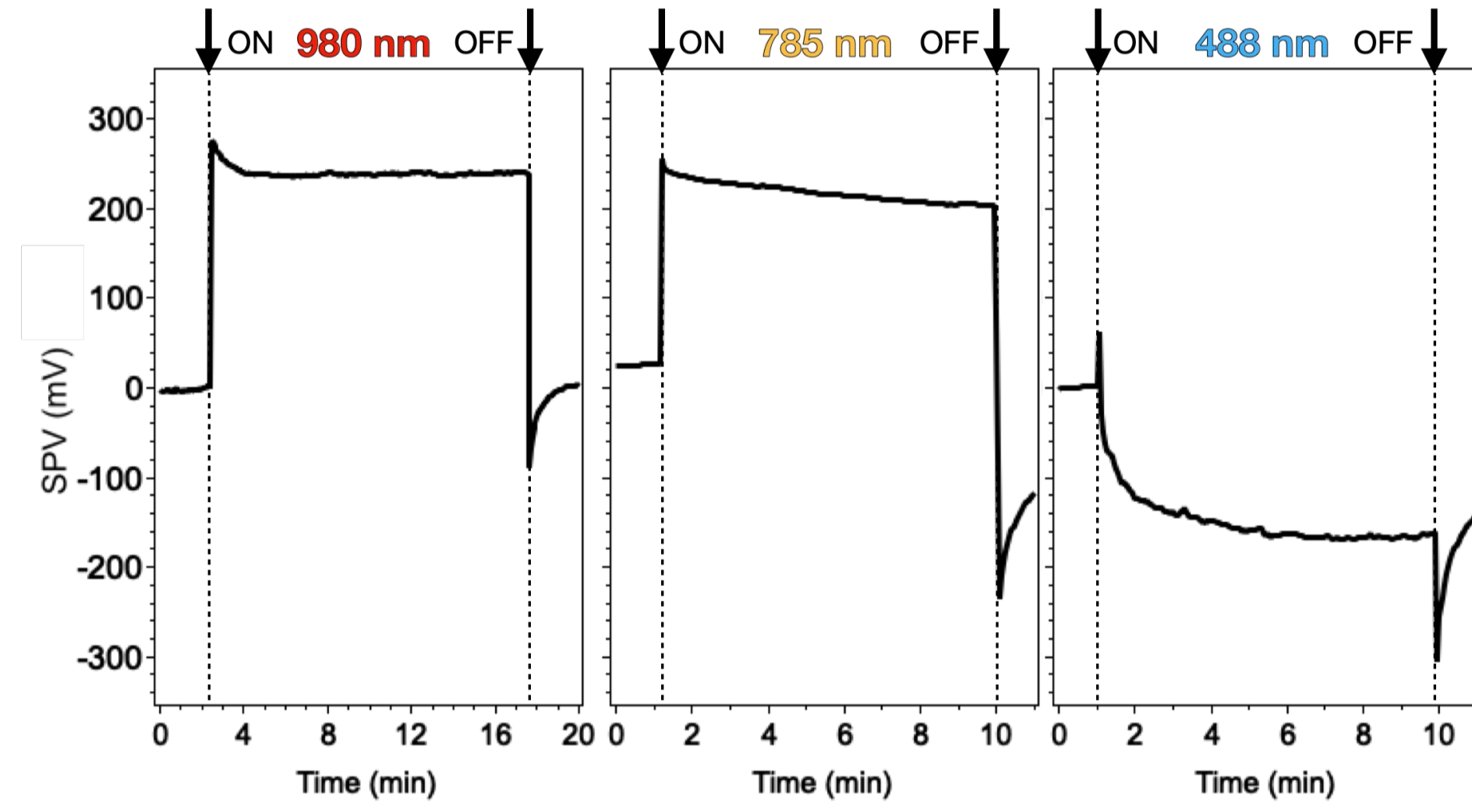
i) MIS-SPV operation mode: chopped light (94Hz), low photon flux density ($\sim 10^{13}$ cm⁻²s⁻¹), possible wavelength range from 500 to 1300 nm

ii) KPFM-SPV operation mode: continuous diode laser illumination at a fixed wavelength (980, 785 and 488 nm) with high photon flux ($\sim 5 \times 10^{17}$ cm⁻²s⁻¹)

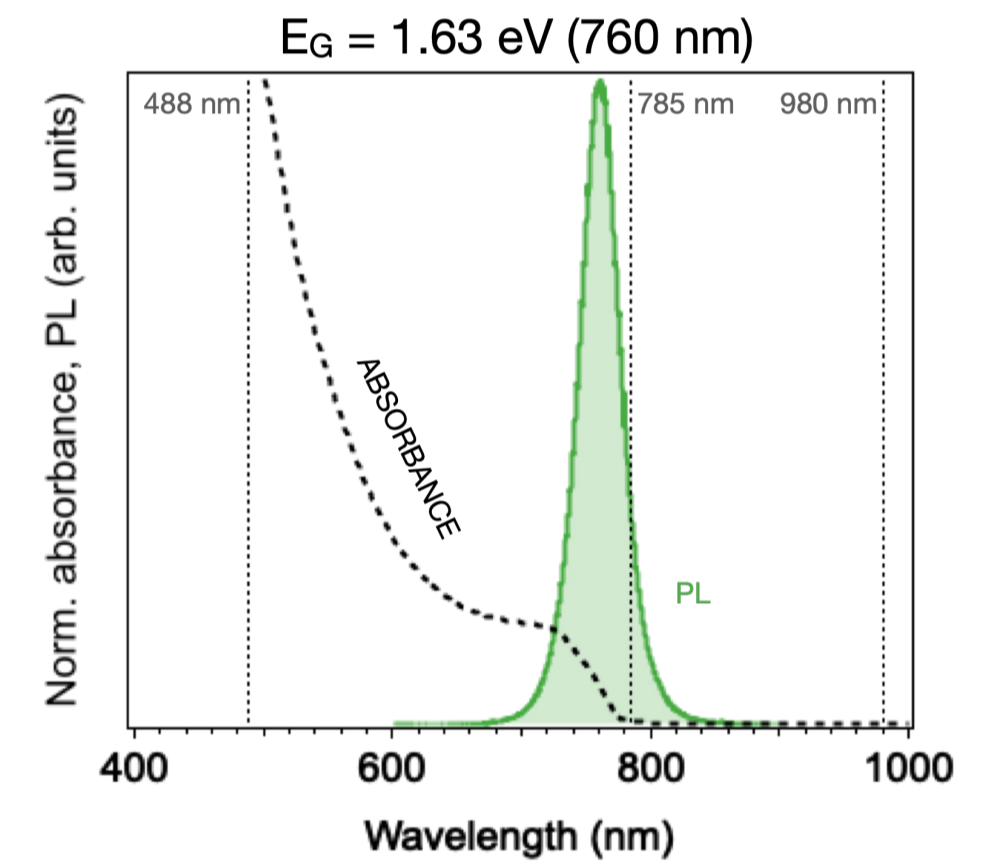
Results and discussion:



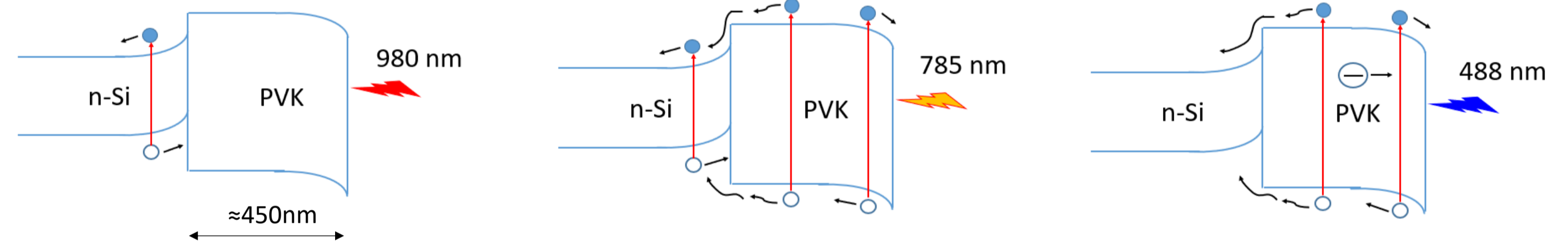
MIS-SPV amplitude (circles) and phase (blue line) spectra of a PVK/n-Si structure measured **a few days after deposition (a)** and **after one year storage in air in the dark (b)**. The amplitude of a bare Si substrate is shown with red squares in (b).



SPV transients measured by KPFM in a sample PVK/n-Si after switching on and off the illumination of three laser diodes with wavelengths 980 nm (a), 785 nm (b) and 488 nm (c). The moments of switching on and off the light are indicated. Reproduced from [3].



PL and absorption spectra of the investigated perovskites.



Spectral range	Absorption in	Observation	Explanation
$\lambda > 800$ nm	Si	KPFM-SPV > 0; MIS-SPV phase in IV th Quadrant	Strong space charge region (SCR) in Si with upward energy band bending
980 nm, Light OFF	-	Negative KPFM-SPV peak and transient toward zero	Detrapping of electrons at the PVK/n-Si interface
800-760 nm	Si, PVK	Step-like increase of the MIS-SPV amplitude	Optical transitions including shallow levels at the PVK/n-Si interface. Increased after one year.
785 nm, Light ON	Si, PVK	KPFM-SPV > 0, slowly decreases	Interface signal dominates. Trapping of negative charges at the interface and/or surface.
785 nm, Light OFF	-	Negative KPFM-SPV peak and slow transient toward zero	Slow detrapping of the negative charges
770-740 nm	PVK	sharp cut-off of the MIS-SPV amplitude	PVK bandgap at 760 nm (1.63 eV, PL) Photons don't reach Si (PVK ≈ "parasitic absorber" [2])
740-500 nm	PVK	MIS-SPV amplitude decreases; MIS-SPV phase decreases in IV th Quadrant; still SPV > 0	Interplay of two MIS-SPV components with nearly opposite phases. i) SPV > 0 (diffusion of carriers to the interface). ii) SPV < 0 (downwards energy band bending at the PVK surface)
488 nm, Light ON	PVK (~50 nm)	Slow negative KPFM-SPV transient	Predominance of the signal from the interface. Creation and movement toward the surface of negative ions – trapped at the surface.
488 nm, Light OFF	-	Further negative KPFM-SPV peak and very slow transient toward zero.	Predominance of the signal from the surface. Slow detrapping of the negative ions

Conclusions:

1. Direct assessment of the optoelectronic properties at the immediate PVK/Si contact.
2. Strong SCR in Si at the PVK/n-Si interface with upward band bending leading to positive SPV.
3. Downward band bending at the PVK surface leading to negative SPV.
4. Increased shallow defect levels at the PVK/n-Si interface due to ageing.
5. Creation and migration of negative ions induced by illumination with 488 nm.
6. Trapping (under illumination) and detrapping (in the dark) of negative ions at the surface.

References:

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- [2] Mariotti S. et al. Direct Silicon Heterostructures with Methylammonium Lead Iodide Perovskite for Photovoltaic Applications, *IEEE J. Photovoltaics* **10** 945–51 (2020)
- [3] Bojar A. et al. Surface photovoltage characterisation of metal halide perovskite on crystalline silicon using Kelvin probe force microscopy and metal-insulator-semiconductor configuration, *EPI Photovoltaics* **13** 18 (2022)

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