Perovskite-silicon tandem solar cells are a promising way for overcoming the single-cell efficiency limit. To date, only a few studies were dedicated to a direct investigation of immediate perovskite-silicon interface. While in most tandem solar cell designs these two materials are not in direct contact, knowledge of the carrier transport and band alignment at their interface would allow for a better understanding of their compatibility and attainable performance levels, guiding the development of perovskite-silicon tandem solar cells in monolithic device architectures with adapted tunnel-recombination junctions between the two sub-cells.

The surface photovoltage (SPV) technique consists of measuring the changes of the surface potential, which are induced by optical generation of free charge carriers, followed by their space redistribution in the sample. It gives information regarding band bending in the sample both at the surface and interfaces, and thus opens the discussion on band alignment between materials.

In this study, we prepared structures made of perovskite layers (about 400 nm thick) deposited onto both p-type and n-type silicon substrates. These were analyzed by means of two set-ups using different operating modes of the SPV technique, the first by Kelvin probe force microscopy (KPFM) and the second with the metal-insulator-semiconductor (MIS) structure operation mode and AC excitation at various frequencies, each providing unique advantages and complementing the other. KPFM allowed to visualize surface potential distribution on a microscale while MIS technique allowed to study SPV spectral dependence.

Our results reveal a relative shift of the perovskite’s Fermi level solely depending on the doping type of the silicon substrate. We also studied the wavelength-dependent surface photovoltage (surface photovoltage spectroscopy) of these samples, which allowed us to effectively vary the probe depth in the sample and discern the contribution from each interface to the overall effect measured under white light illumination. Depending on where the photocarriers are generated, different SPV signals are observed: at the perovskite/Si interface, the signal depends on Si doping type, while at the surface the SPV is always negative indicating downward surface band bending. This is confirmed by analyzing SPV phase measured in the AC MIS mode. In addition, distinction between slow and fast processes contributing to measured SPV was possible. It has been observed, that with decreasing the illumination wavelength, the processes causing SPV become slower, which can indicate that high energy photons not only generate electronic photocarriers but can also induce chemical changes with creation of defects or ionic species that also modify the measured SPV.