



**HAL**  
open science

## Electronic Properties of Metal Halide Perovskites and their Interfaces with Charge Extraction Layers in Lateral Heterojunction Configuration

Sean P. Dunfield, Aleksandra Bojar, Stefania Cacovich, Mathieu Frégnaux, Talysa Klein, Rosemary Bramante, Fei Zhang, Davide Regaldo, Vincent Dufoulon, Jean-Baptiste Puel, et al.

### ► To cite this version:

Sean P. Dunfield, Aleksandra Bojar, Stefania Cacovich, Mathieu Frégnaux, Talysa Klein, et al.. Electronic Properties of Metal Halide Perovskites and their Interfaces with Charge Extraction Layers in Lateral Heterojunction Configuration. Journées Nationales de Spectroscopies de PhotoEmission (JNSPE 2022), May 2022, Dijon, France. EDP Sciences, Journées Nationales des Spectroscopies de Photoémission (JNSPE 2022). hal-03878570

**HAL Id: hal-03878570**

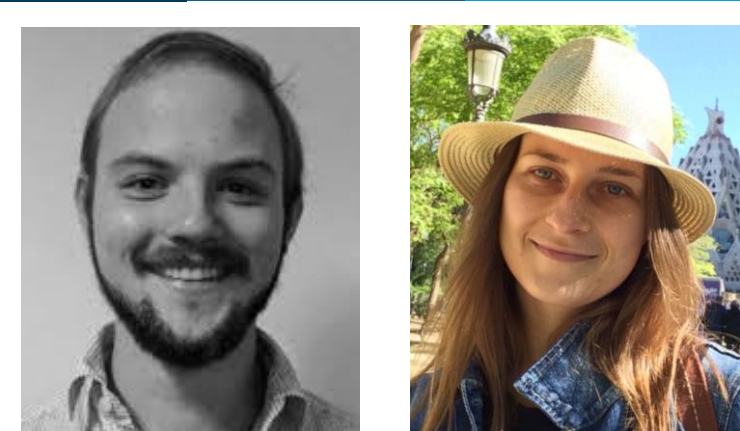
**<https://hal.science/hal-03878570>**

Submitted on 3 Dec 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.





[sdunfield@eng.ucsd.edu](mailto:sdunfield@eng.ucsd.edu)  
[aleksandra.bojar@cnrs.fr](mailto:aleksandra.bojar@cnrs.fr)  
[philip.schulz@cnrs.fr](mailto:philip.schulz@cnrs.fr)



Sean Dunfield<sup>a</sup>, Aleksandra Bojar<sup>b</sup>, Stefania Cacovich<sup>b</sup>, Mathieu Frégnaux<sup>c</sup>, Talysa Klein<sup>a</sup>, Rosemary Bramante<sup>a</sup>, Fei Zhang<sup>a</sup>, Davide Regaldo<sup>b</sup>, Vincent Dufoulon<sup>b</sup>, Jean-Baptiste Puel<sup>d</sup>, Glenn Teeter<sup>a</sup>, Joseph Luther<sup>a</sup>, Muriel Bouttemy<sup>c</sup>, Dennis Nordlund<sup>e</sup>, Kai Zhu<sup>a</sup>, David Moore<sup>a</sup>, Maikel van Hest<sup>a</sup>, Jean-Paul Kleider<sup>f</sup>, Joseph Berry<sup>a</sup>, Philip Schulz<sup>b</sup>

<sup>a</sup> National Renewable Energy Laboratory, Golden CO, 80401, USA

<sup>b</sup> CNRS, Institut Photovoltaïque d'Île de France (IPVF), Palaiseau, 91120, France

<sup>c</sup> Institut Lavoisier de Versailles (ILV), Université de Versailles-Saint-Quentin-en-Yvelines, Université Paris-Saclay, CNRS, UMR 8180, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France

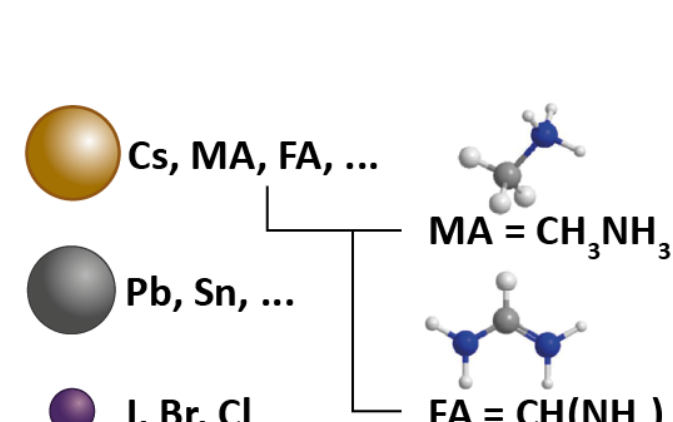
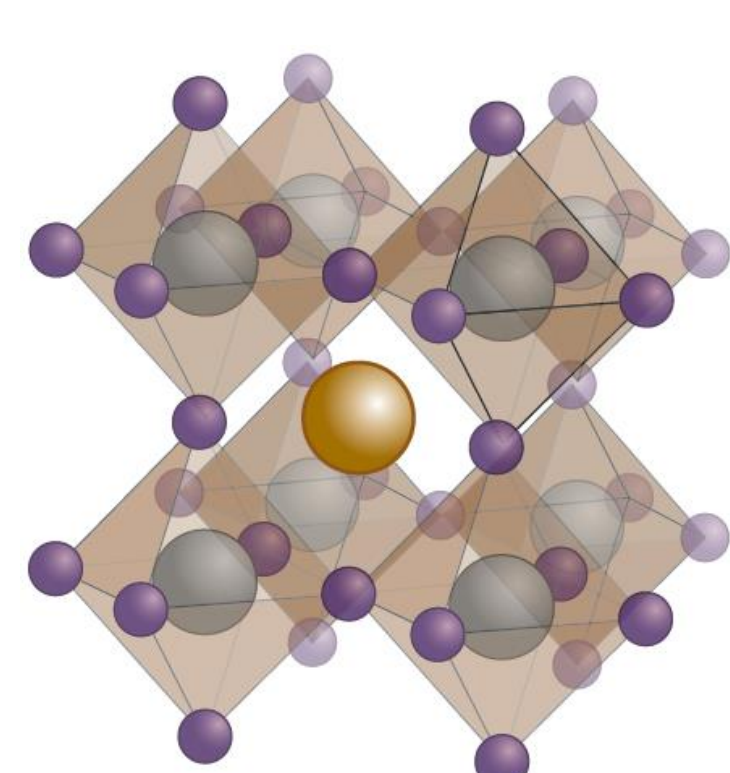
<sup>d</sup> EDF R&D, 91120 Palaiseau, France

<sup>e</sup> SLAC National Accelerator Laboratory, Menlo Park CA, 94205, USA

<sup>f</sup> Laboratoire de Génie Électrique et Électronique de Paris (GeePS), CNRS UMR 8507, Université Paris-Sud, Université Paris-Saclay, 91192 Gif-sur-Yvette Cedex, France

# Electronic Properties of Metal Halide Perovskites and their Interfaces with Charge Extraction Layers in Lateral Heterojunction Configuration

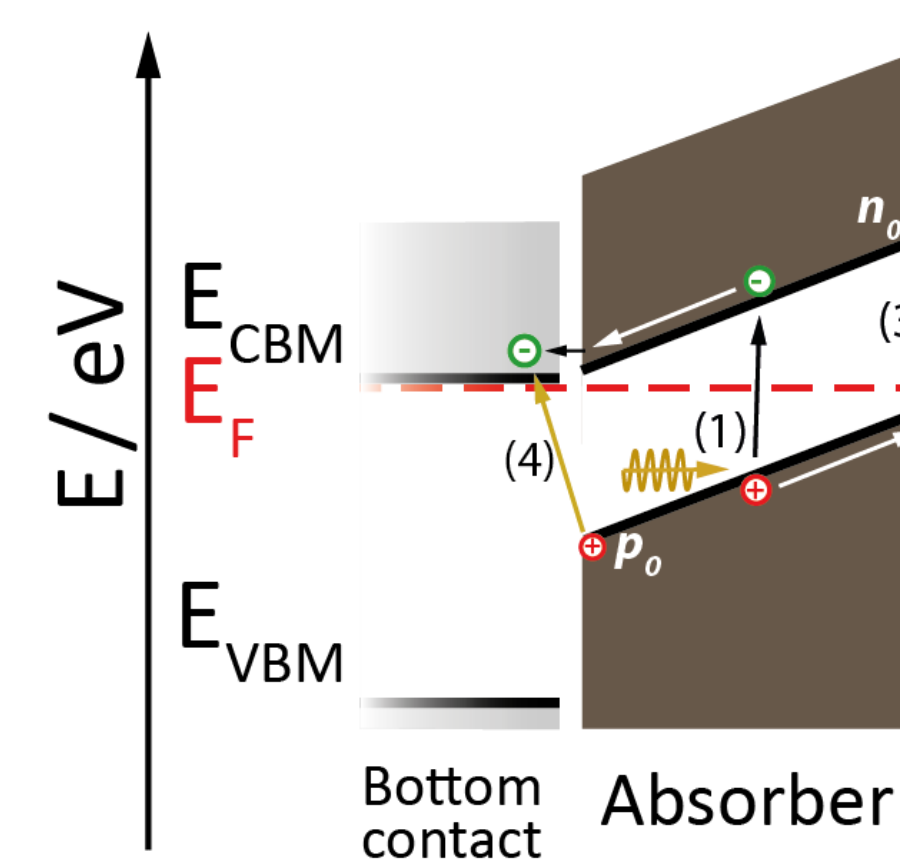
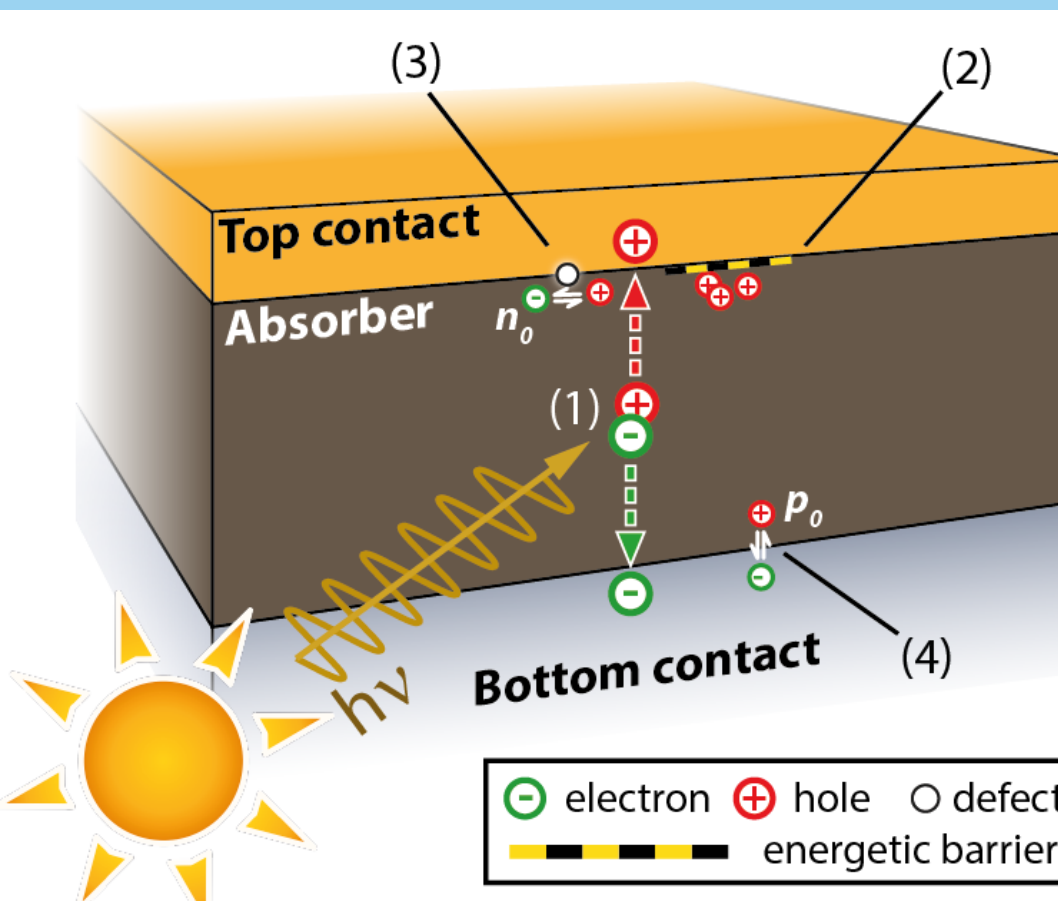
## Metal Halide Perovskites: Applications and Interfaces



Hybrid organic-inorganic metal halide perovskite (MHP) with complex chemical structure  $\text{ABX}_3$

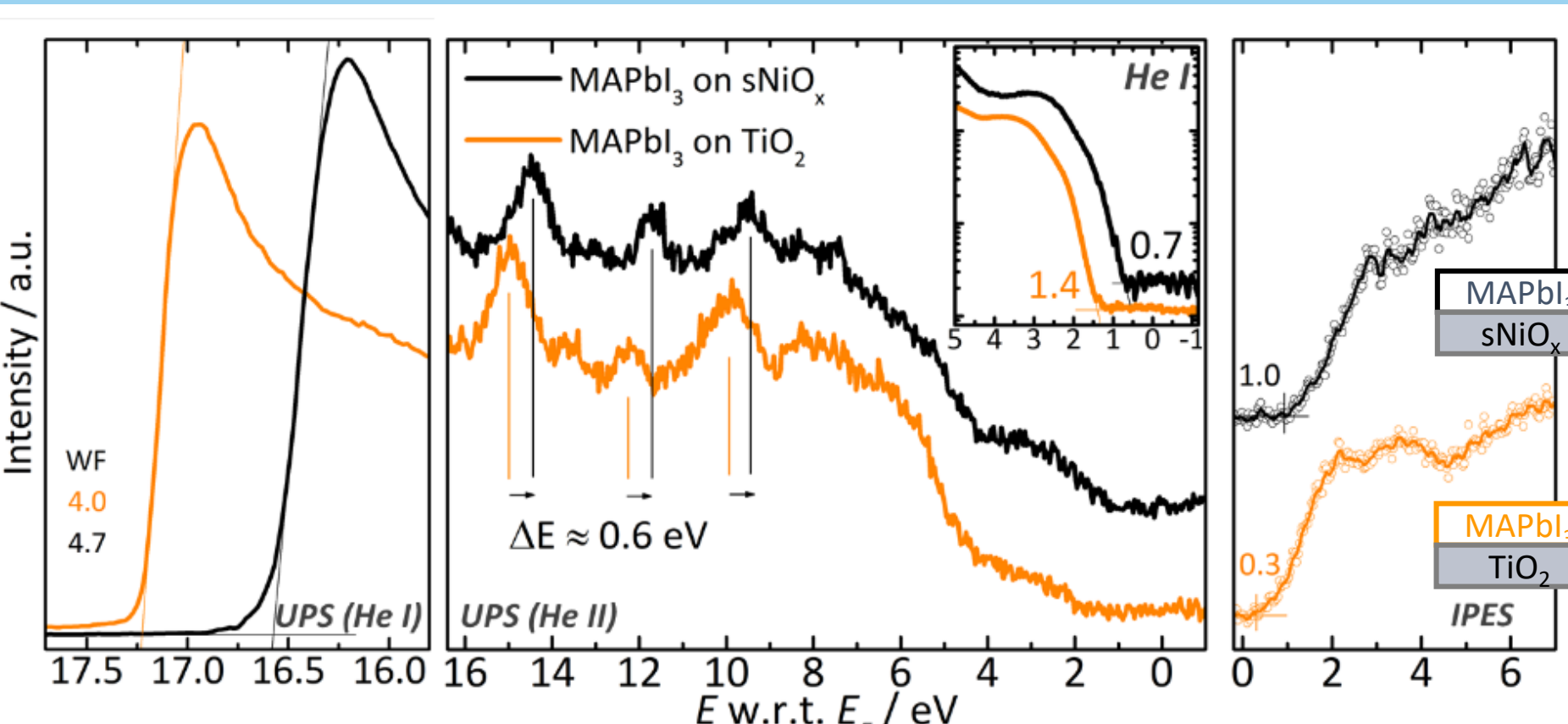
Semiconductor with unique combination of optoelectronic and mechanical properties<sup>1</sup>

Breakthrough application in photovoltaics: Perovskite solar cells (PSC)



- Relevant loss-channels:
- (1) Photoexcitation and transport to interface
  - (2) Band misalignment of as barrier for charge extraction
  - (3) Recombination at interface defect states
  - (4) Back-recombination
- Predominantly losses at interface<sup>2,3</sup>

## Substrate-dependent Fermi Level Alignment and Lateral Heterojunction (LHJ)

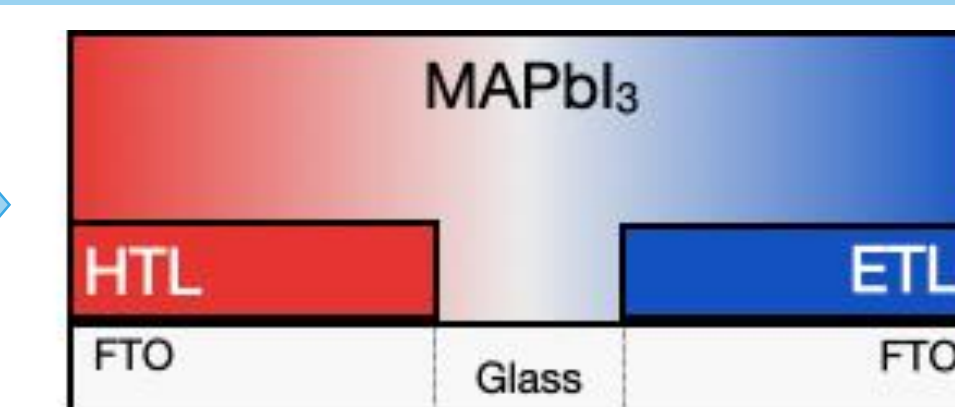
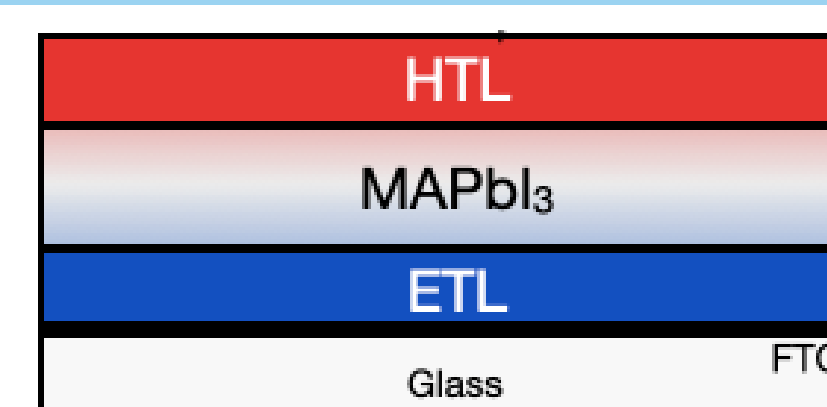


Combined ultraviolet and inverse photoemission spectroscopy (UPS/IPES)<sup>4</sup>:

Optoelectronic properties of MHP can be altered by the substrate (or selective contact) underneath

Position of Fermi level ( $E_F$ ) at the surface of the perovskite film ( $\text{MAPbI}_3$ , 400 nm) changes on different substrate, with  $E_F$  close to the perovskite conduction band on  $\text{TiO}_2$  and in a mid-gap position on  $\text{NiO}$

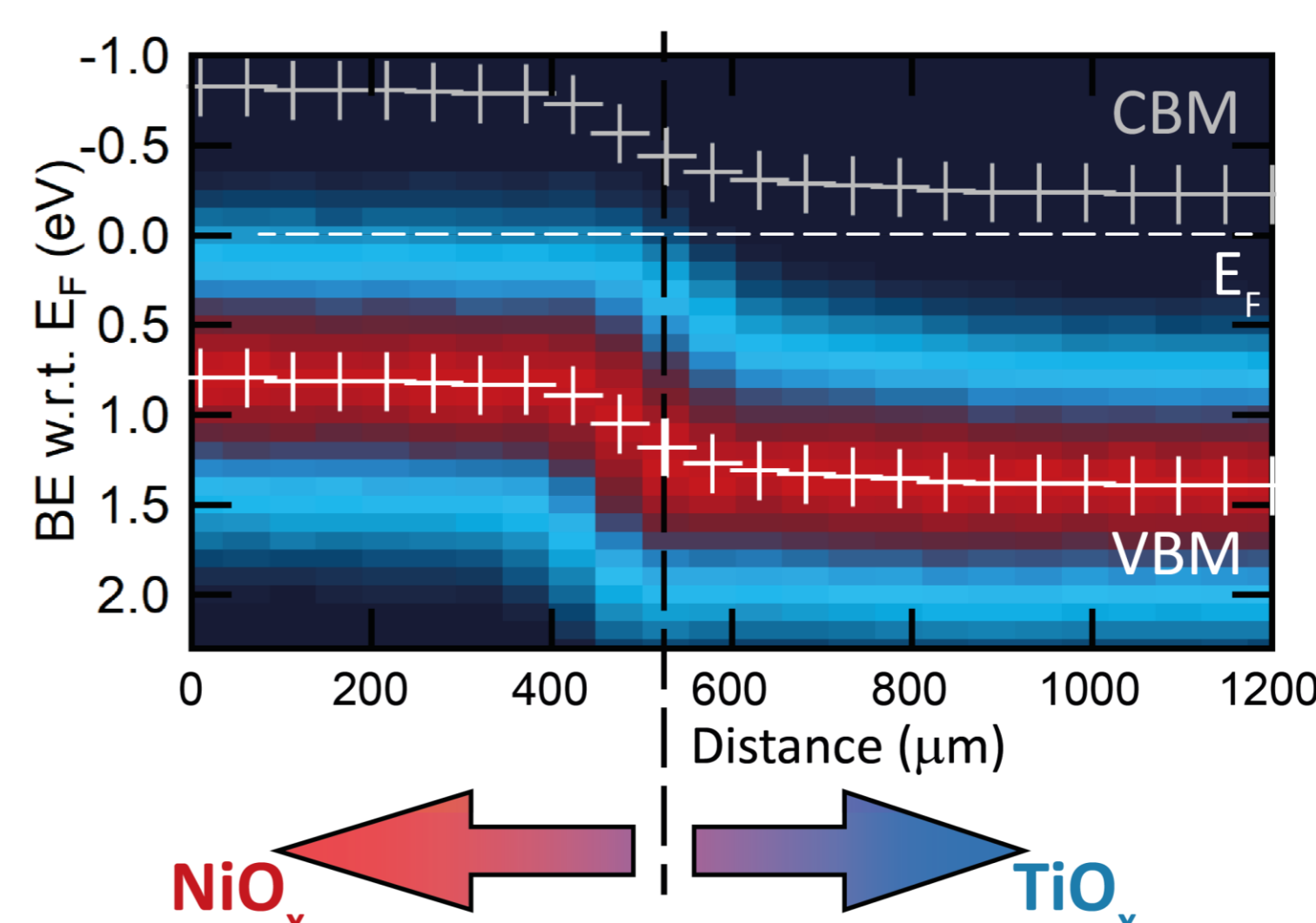
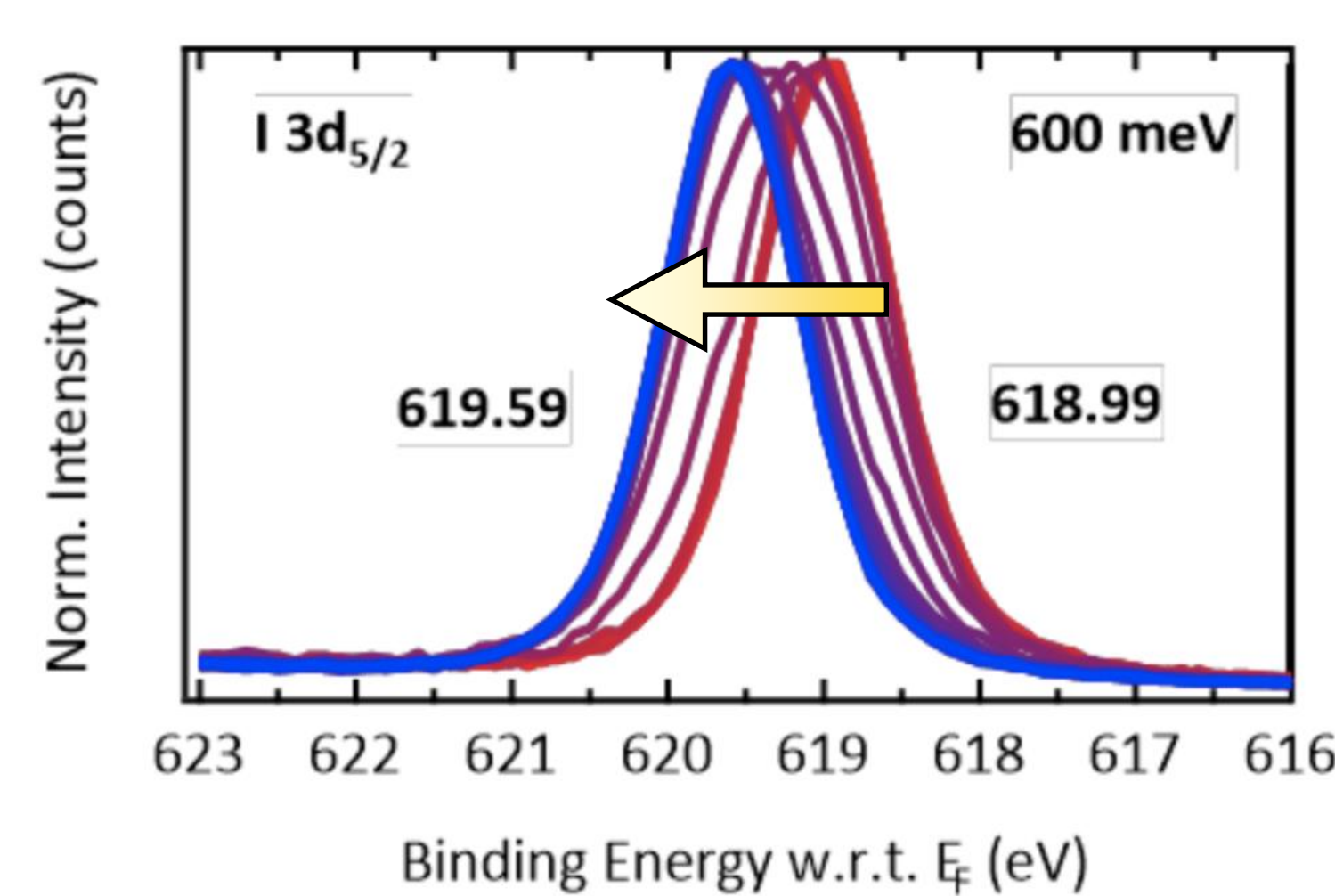
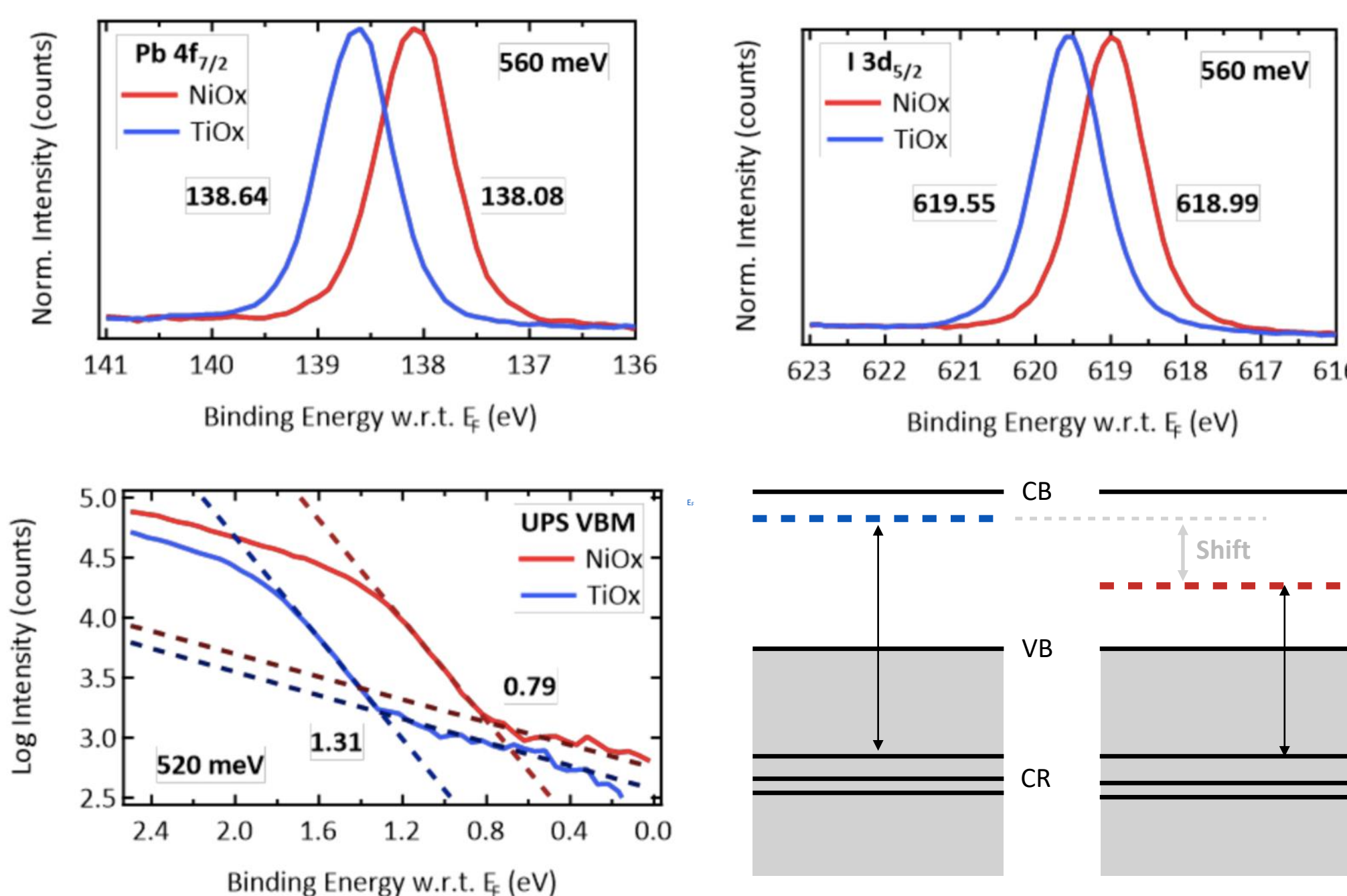
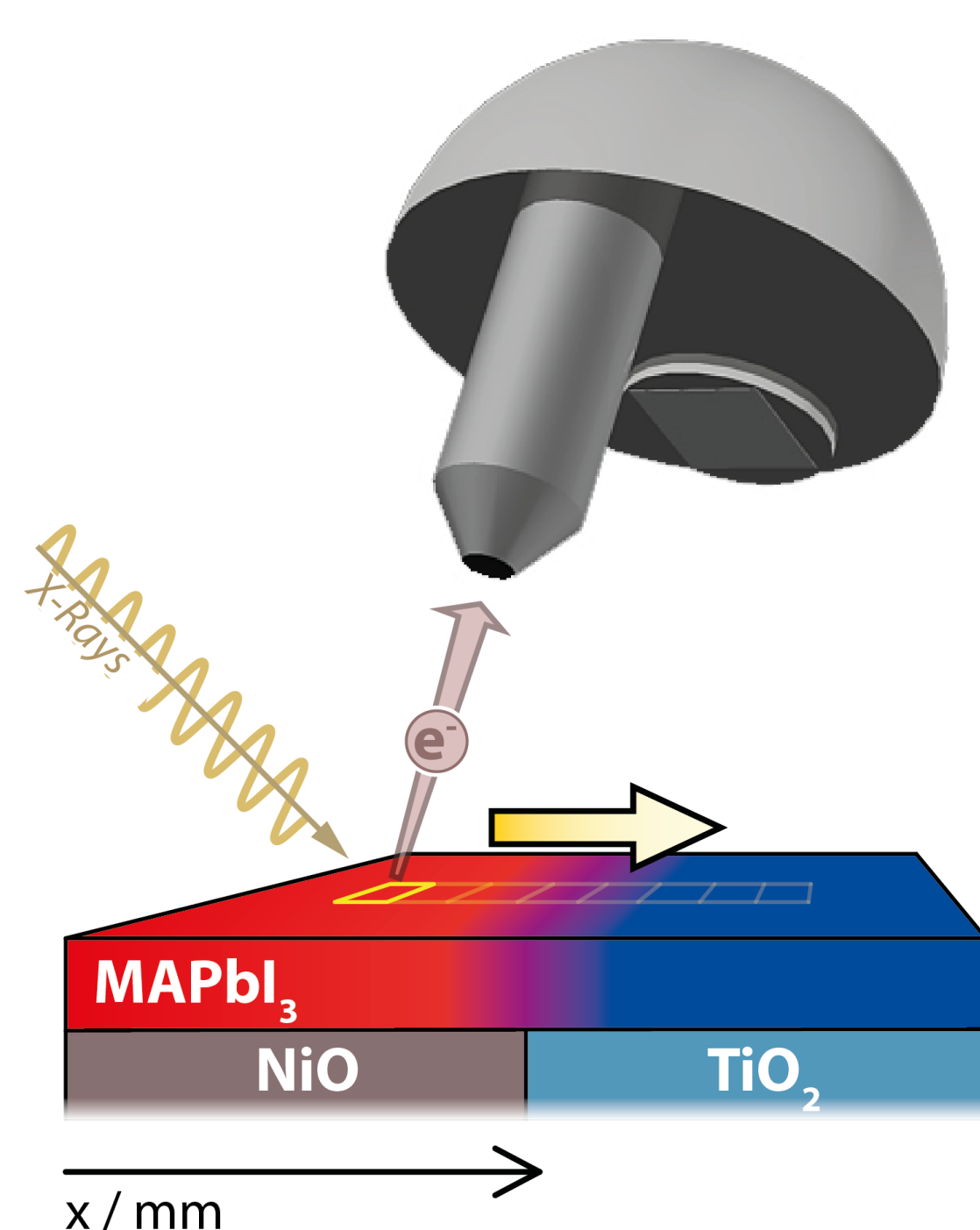
Need to track interface formation and energy level alignment



Transition from common, vertically stacked sample geometry to lateral heterojunction architecture<sup>5</sup>

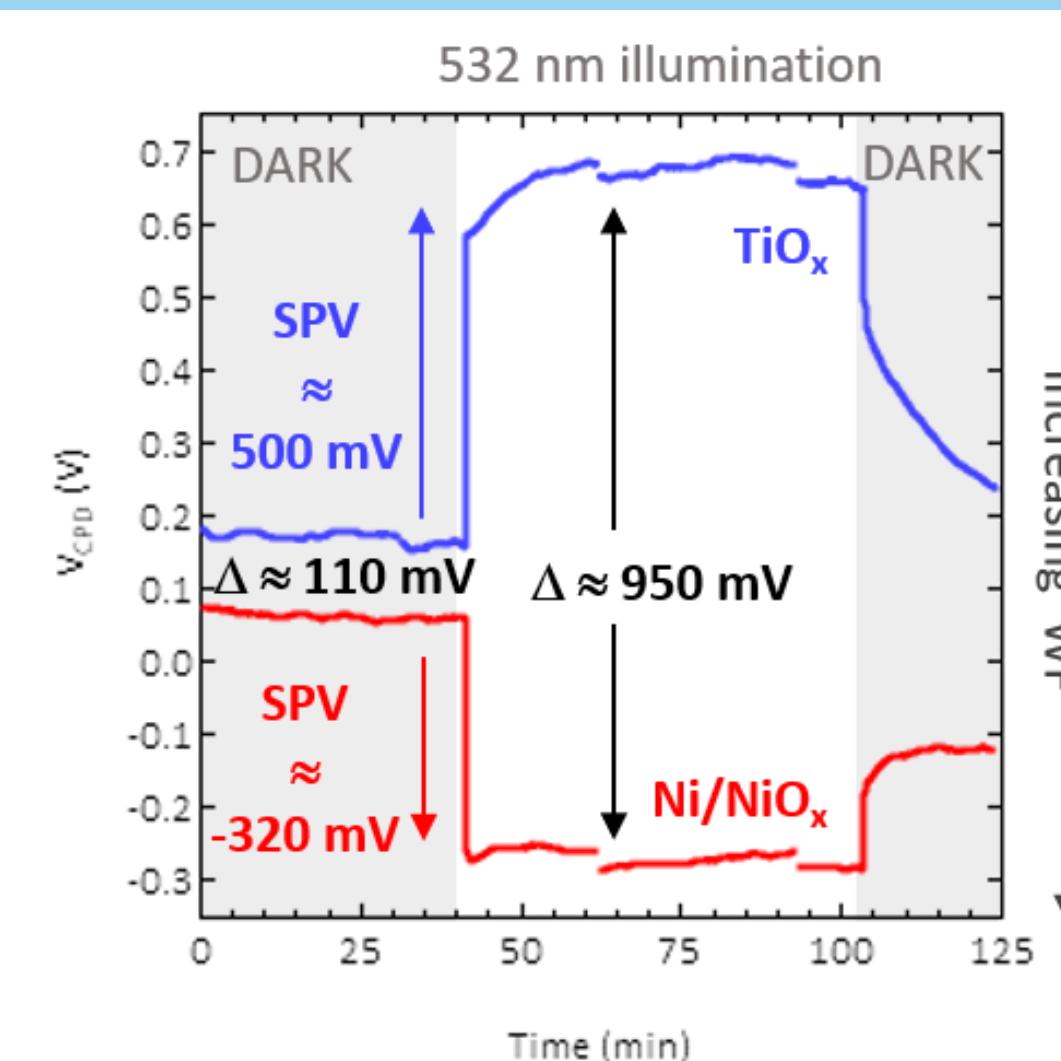
Access to surface electronic and chemical properties across channel

## Photoelectron Spectroscopy across LHJ channel

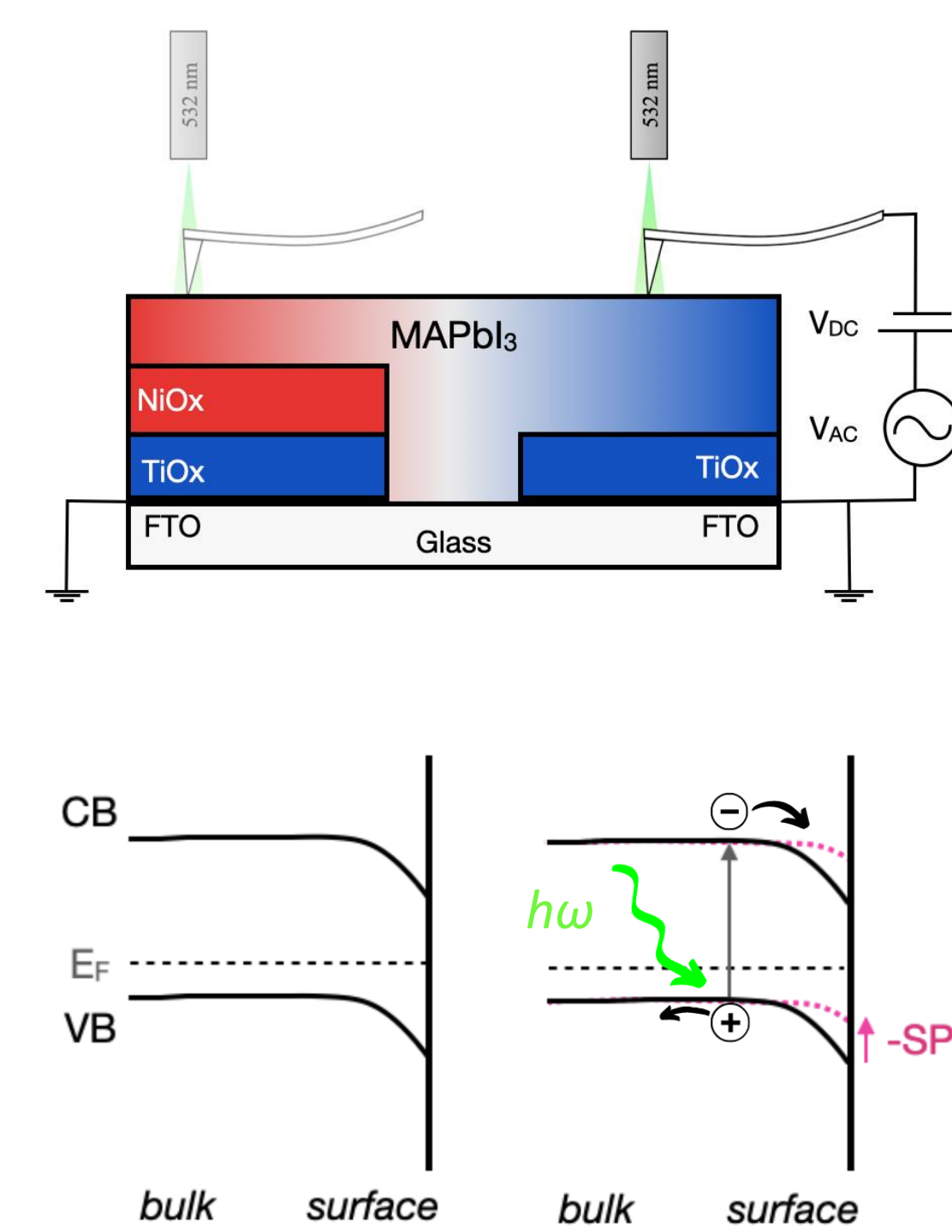


- Lateral contact design as in interdigitated back contacts
- Perovskite deposition on top
- XPS/UPS data acquisition at end points
- Scanning PES (XPS,  $\text{I } 3d_{5/2}$ ) across lateral heterojunction (LHJ)
- Drift-diffusion modelling to determine origin of surface potential<sup>5,6</sup>
- Observed profile of surface potential requires low doping concentration in MHP ( $<10^{13} \text{ cm}^{-3}$ )

## Complementary Kelvin Probe Force Microscopy



- Assess surface potential / work function
- Measurement in dark and under illumination to capture surface photovoltage (SPV)
- Significant difference in SPV between MHP on  $\text{TiO}_x$  vs MHP on  $\text{NiO}_x$  indicates change of carrier extraction at interface<sup>5</sup>



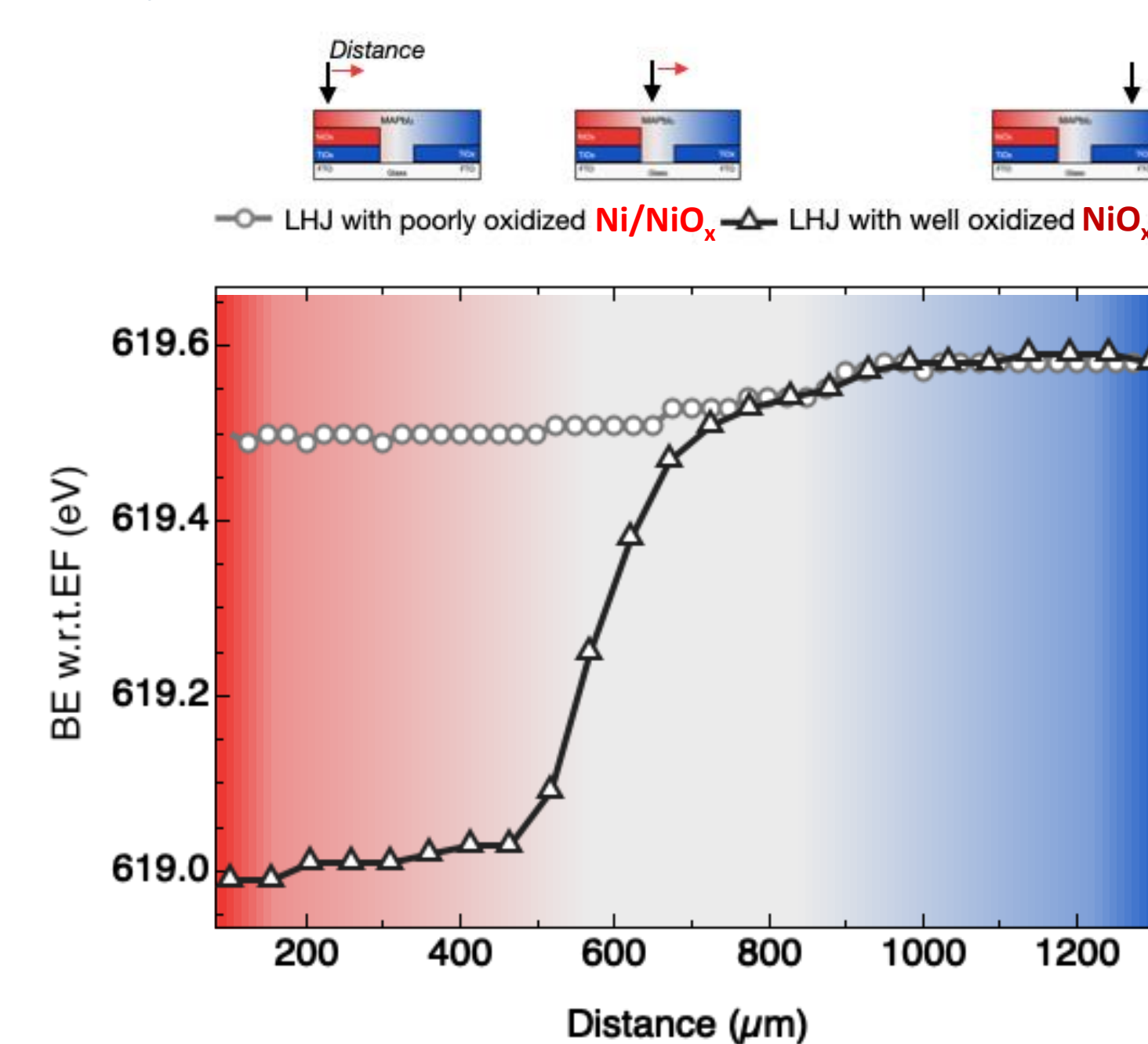
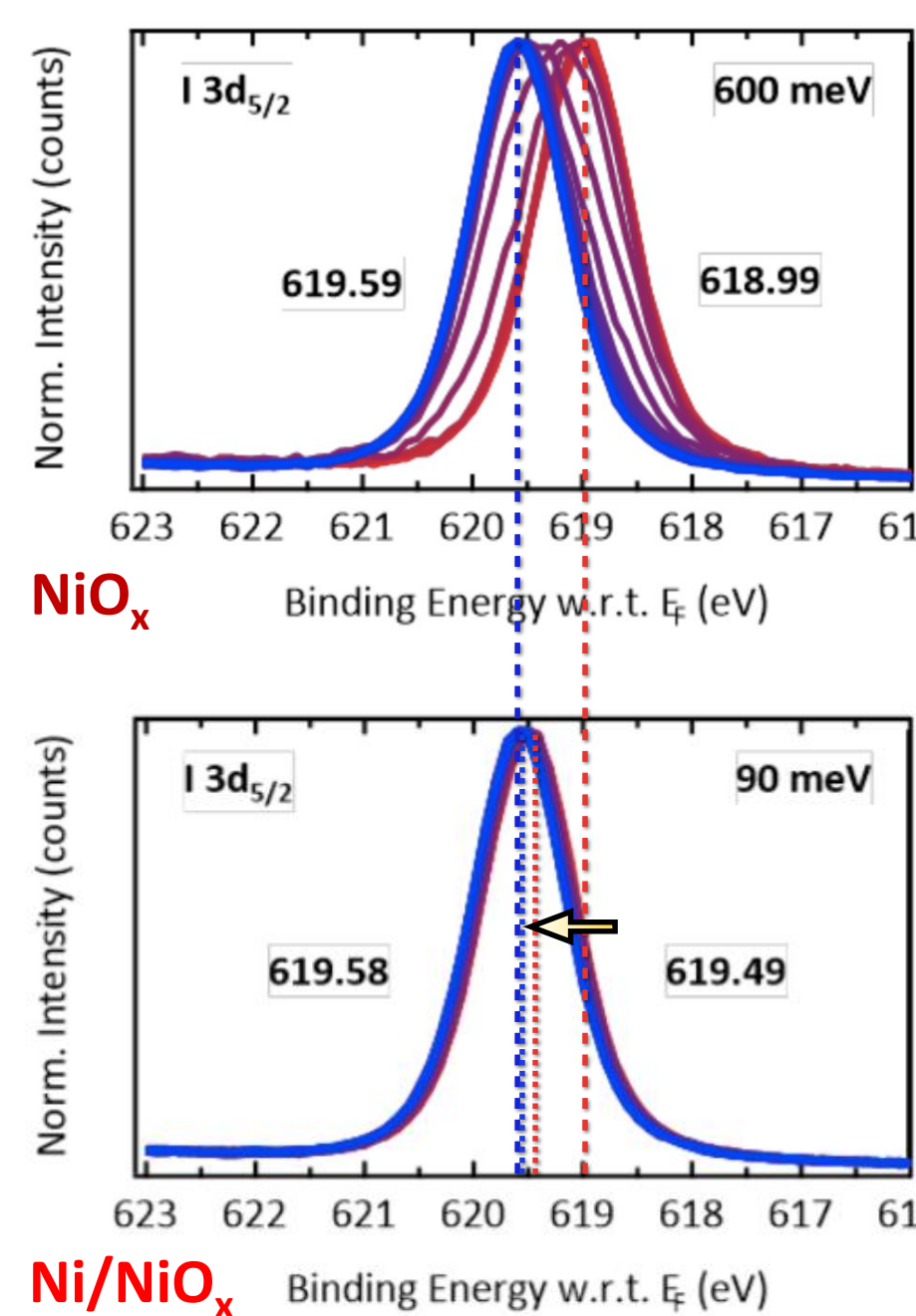
## Modified Charge Selectivity at $\text{NiO}_x$ Contact

Fully oxidized  $\text{NiO}_x$  at 300°C / 120 min anneal

Oxygen-deficient  $\text{Ni/NiO}_x$  at 275°C / 30 min anneal

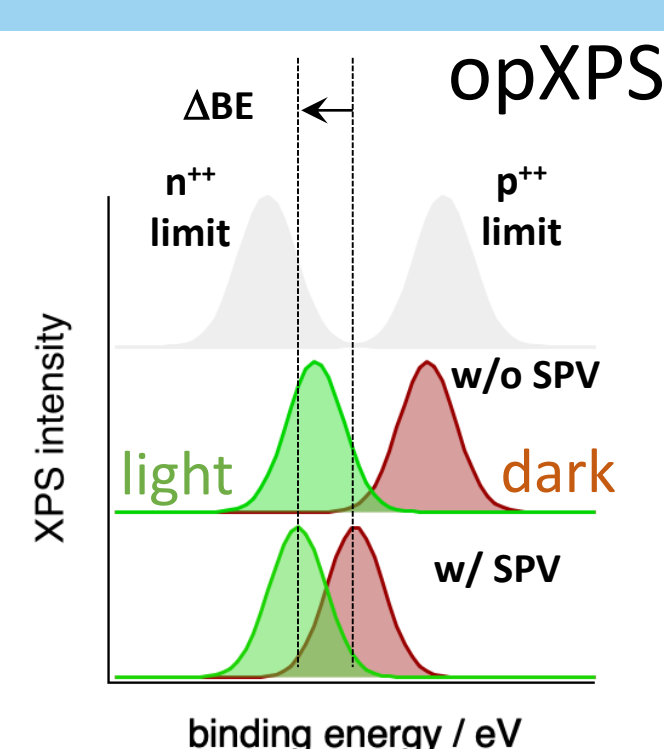
Adaptation of contact selectivity by variation of  $\text{NiO}_x$  oxidation level through controlled annealing

Reduced shift of  $E_F$  in gap for poorly oxidized  $\text{Ni/NiO}_x$  in line with results of higher recombination seen in photoluminescence measurements<sup>5</sup>



## Conclusion and Next Steps

- Charge selective contacts shift the Fermi level in metal halide perovskites (MHPs)
- Effect is readily observable because of low defect and doping concentrations in the MHP
- Contact selectivity determines carrier extraction across MHP/contact interfaces
- Tailoring charge selective contacts to design MHP-based lateral heterojunction devices
- Operando measurements<sup>7</sup> (opXPS & KPFM) to track dynamic effects and potential ion migration
- Access to buried interfaces via HAXPES measurements



## References

- D. Egger et al. *Adv. Mater.* **2018**, *30*, 1800691
- P. Schulz *ACS Energy Lett.* **2018**, *3*, 1287–1293
- P. Schulz, D. Cahen, A. Kahn. *Chem. Rev.* **2019**, *119*, 3349–3417
- P. Schulz, et al., *Adv. Mater. Interfaces* **2015**, *2*, 1400532
- S. Dunfield, A. Bojar, et al., *Cell Rep. Phys. Sci.* **2021**, *2*, 100520
- D. Regaldo, A. Bojar, et al., *Prog. Photovolt.: Res. Appl.* **2021** <https://doi.org/10.1002/pip.3529>
- G. Teeter, P. Schulz, *Photoelectron Spectroscopy Methods in Solar Cell Research*, **2020** [https://doi.org/10.1049/PBPO166E\\_ch12](https://doi.org/10.1049/PBPO166E_ch12)