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Effects of $CdCl_2$ treatment on the local electronic properties of polycrystalline CdTe measured with photoemission electron microscopy

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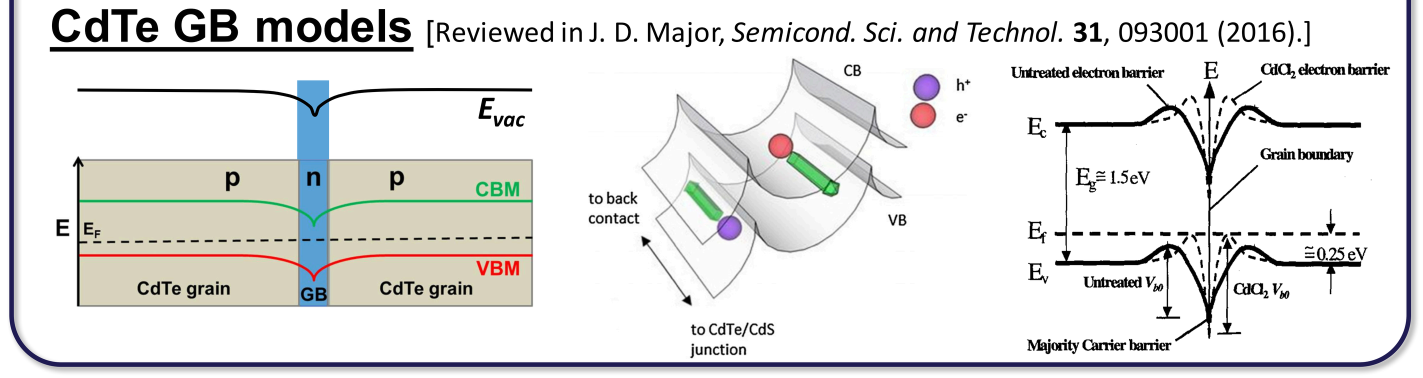
Introduction

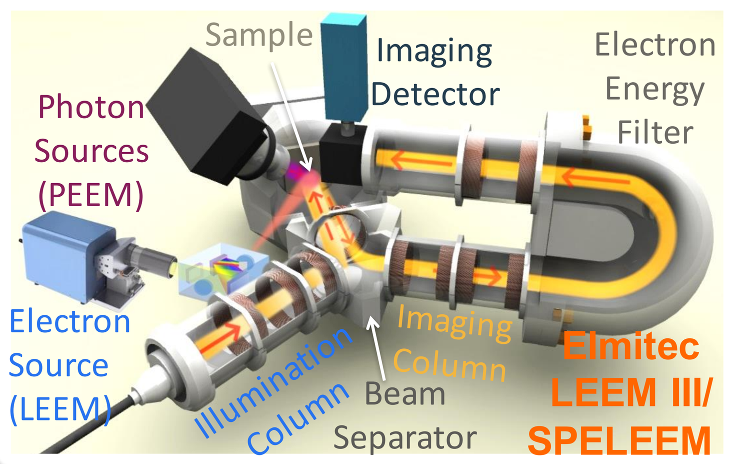
Cadmium telluride (CdTe) is a polycrystalline photovoltaic (PV) material that has recently achieved power conversion efficiencies (21.5%) in research cells rivaling those of multicrystalline silicon. Further improvement of CdTe PV technology requires surpassing current limits in our understanding of fundamental mechanisms that influence processing-structure-property-performance relationships in CdTe. In particular, the influence of grain-boundary (GB) limitations and nano- or microscale nonuniformities have been identified as issues needing improved understanding.

CdTe GB models [Reviewed in J. D. Major, *Semicond. Sci. and Technol.* **31**, 093001 (2016).]



Objective and approach

- **Objective:** Determine processing-structure-property-performance-relationships critical for improving thin-film PV materials and devices.
- **Key Question(s):** How does $CdCl_2$ treatment, a widely-used *processing* step, influence the local *electronic structure* of CdTe thin films? Does oxygen (via air exposure) impact this step?
- **Approach:** Leverage a highly interdisciplinary team to develop and apply a *new metrology tool* – spec-PELEEM – to measure nanoscale chemical and electronic structure of PV materials and devices.



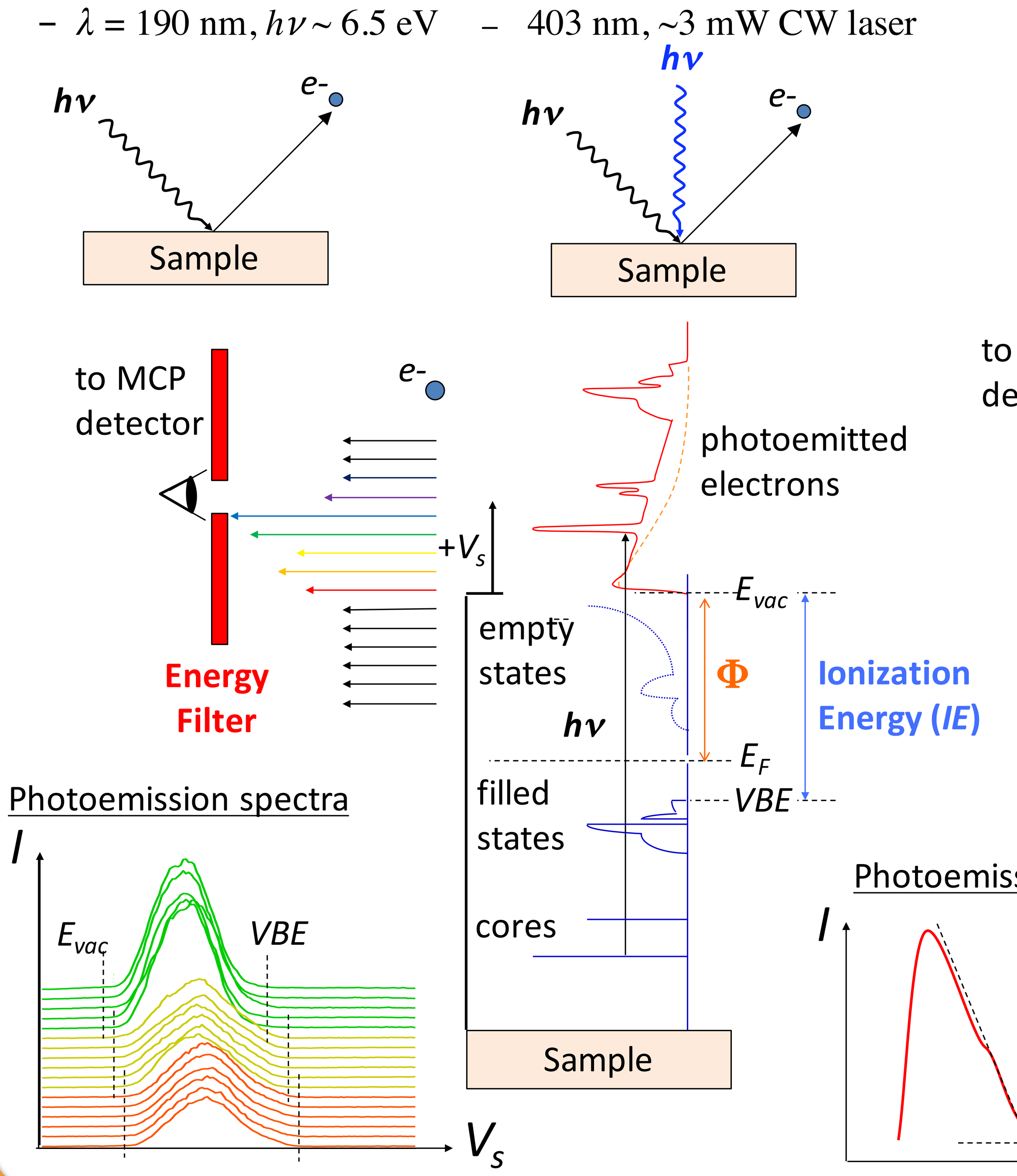
SPELEEM Features
- Resolution:
  - 5-10 nm spatial
  - 0.2-0.5 eV spectral
- Low-energy electron diffraction
- Electron/Photon/ Thermal excitation
- Real-time imaging, in-situ growth

Measurement
- Topology
- Chem./Electron. Structure
- Surface Crystallography
- Phonons/ Plasmons
- Carrier/Field Distribution

Principles and methods: Spectroscopic Photoemission Electron Microscopy (PEEM)

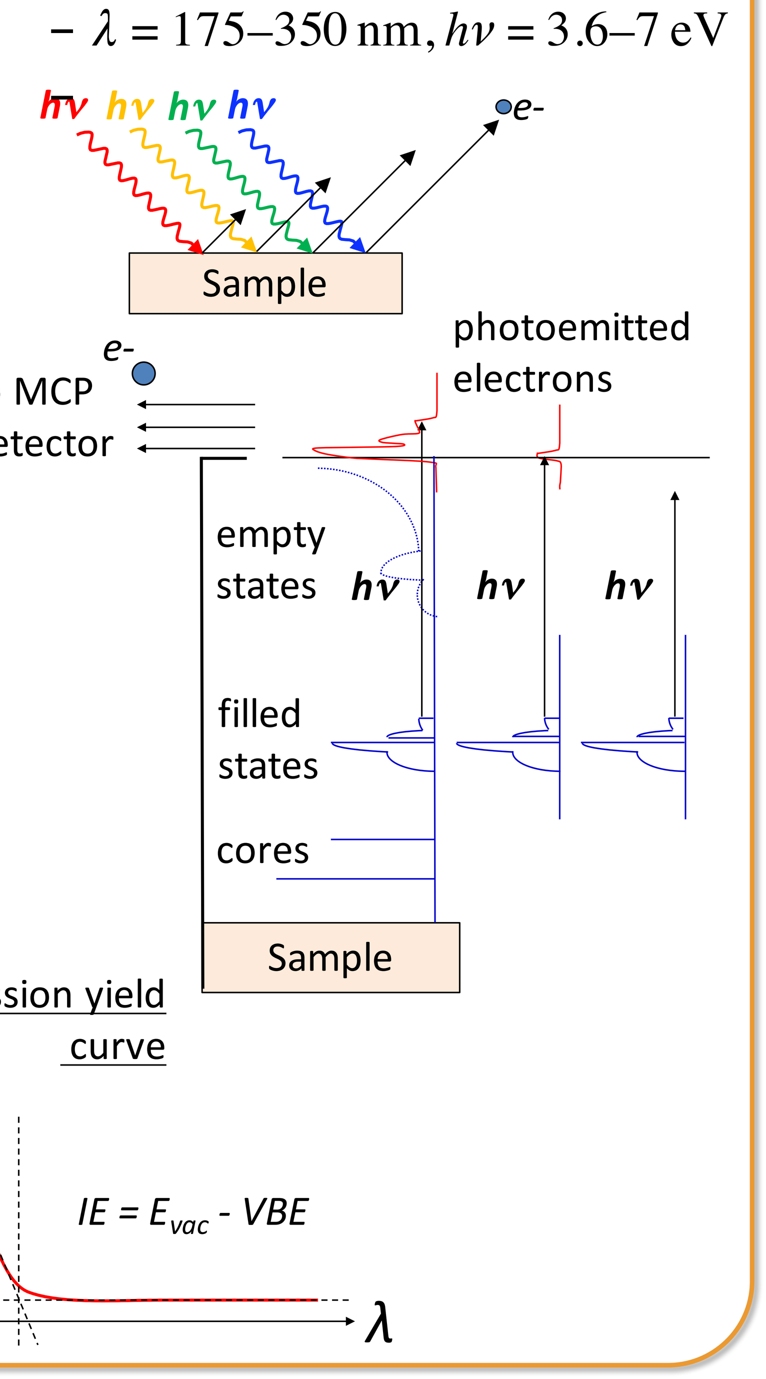
Local Photoemission Spectroscopy (PES) spectra

- Fixed energy, PES
  - $\lambda = 190$ nm, $h\nu \sim 6.5$ eV
- PES + Surface photovoltage (SPV)
  - 403 nm, ~3 mW CW laser



Local Photoemission Yield (PEY)

- Variable energy, PEY
  - $\lambda = 175–350$ nm, $h\nu = 3.6–7$ eV



Results & Discussion

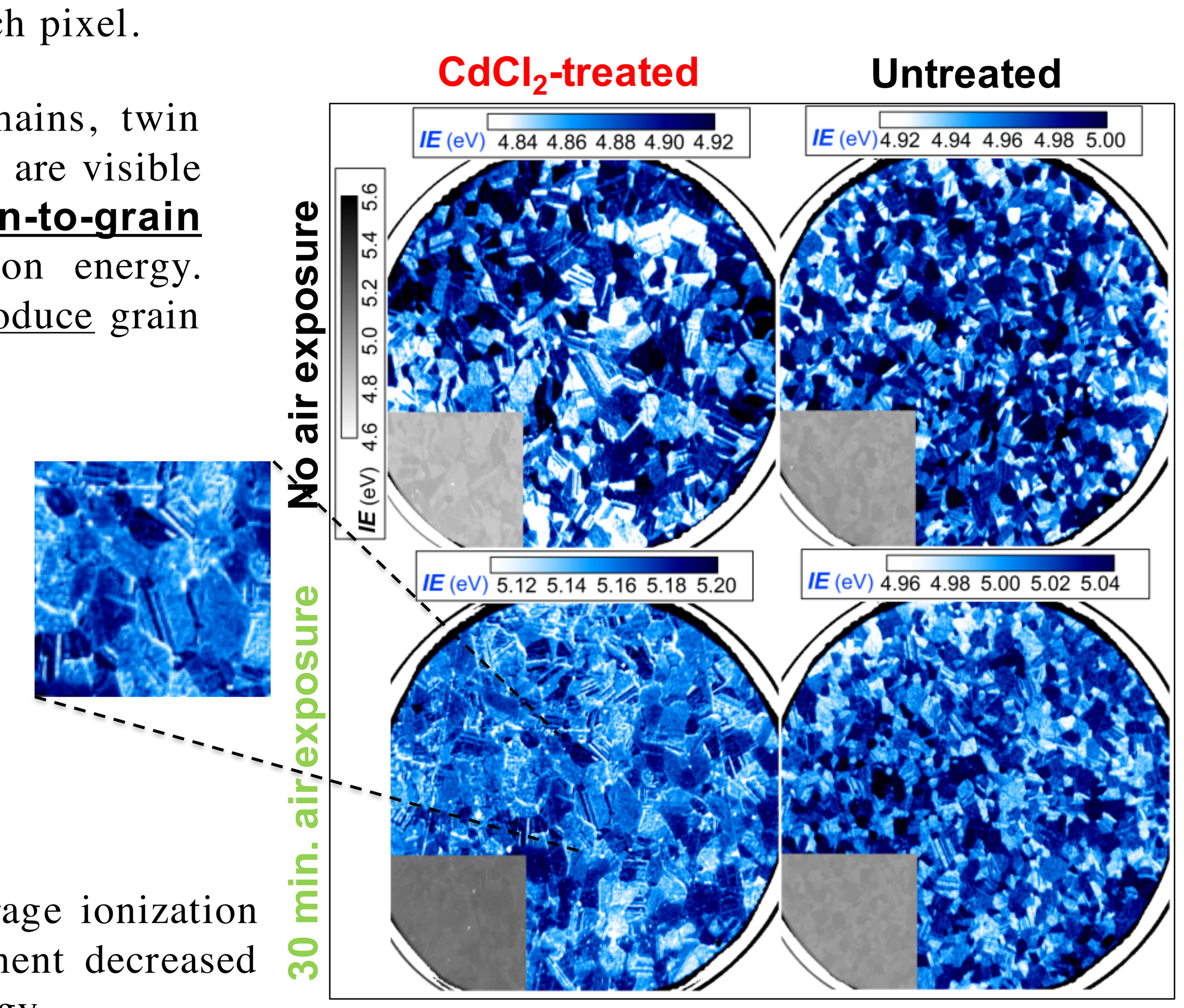
Local ionization energy (PEY) : Intensity (I) vs. Wavelength (λ)

–Take a set of images while sequentially varying the wavelength (λ). Extract an ionization energy (IE) value for each pixel.

Microcrystalline grain domains, twin boundaries, & polish marks are visible in all maps, as is **grain-to-grain variation** of the ionization energy. $CdCl_2$ treatment did not produce grain boundary contrast.

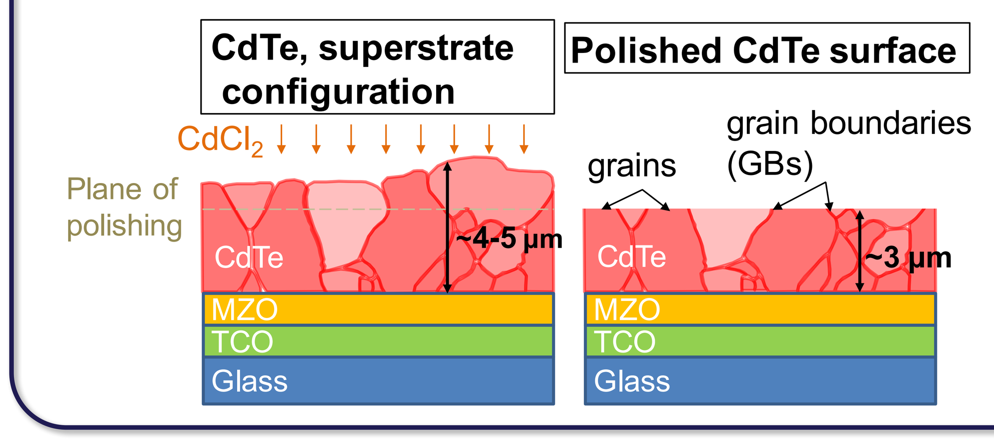
$CdCl_2$ treatment and air exposure produced grain (GB) boundary contrast consistent with scanning probe measurement of activated grain boundaries.

Oxygen increased the average ionization energy while $CdCl_2$ treatment decreased the average ionization energy.



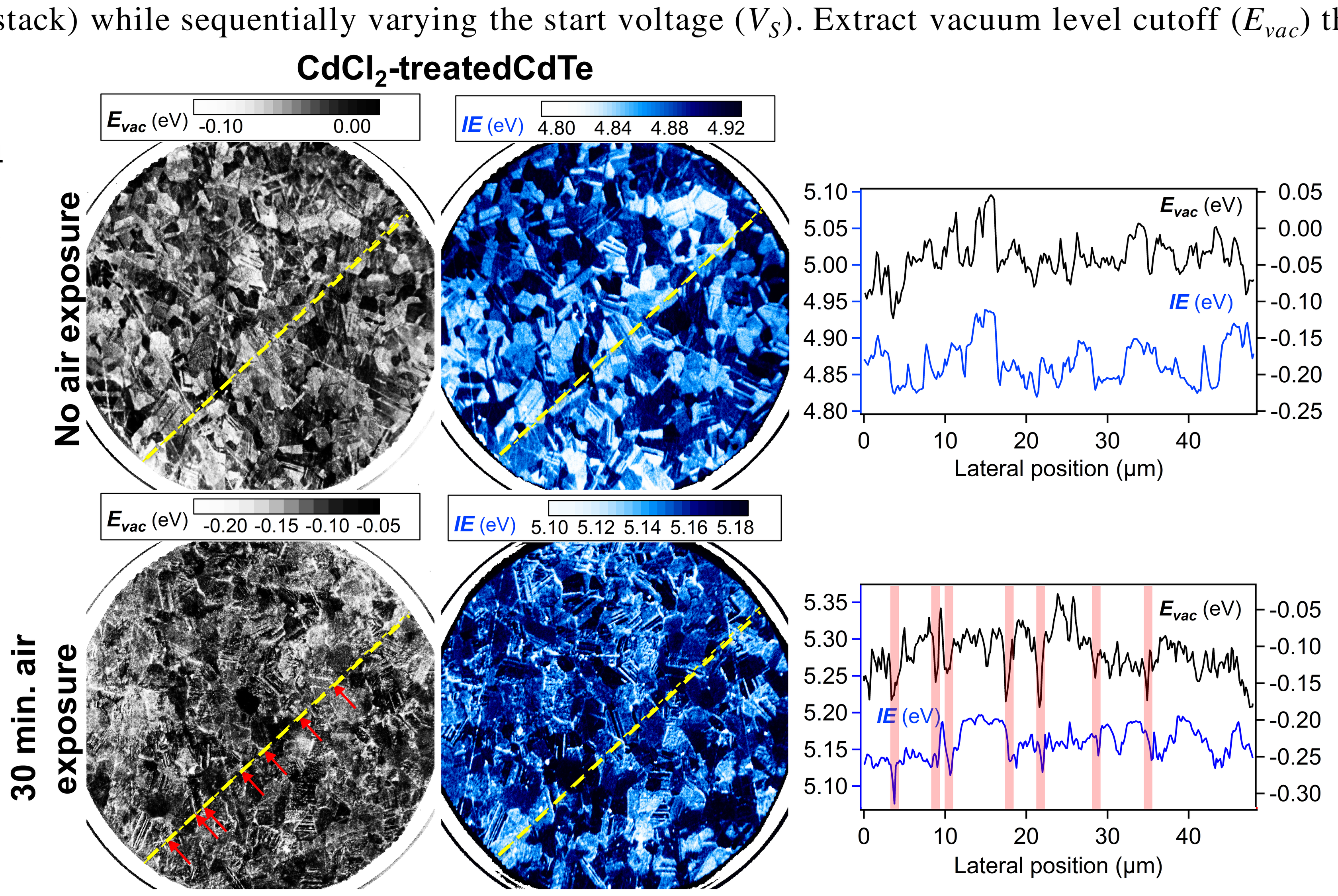
Sample preparation protocol

- NSG TEC 10 glass superstrates coated with transparent conducting oxide (TCO):
  - $SnO_2/SiO_2/SnO_2$:F
- 100 nm $Mg_{0.23}Zn_{0.77}O$ (MZO) window layer
- 4-5 μm closed-space sublimation (CSS) CdTe
- CdTe films are mechanically polished
- Low-energy ion desorption step:
  - 50 eV Ar^+ ions / 10–20 min / ~0.1-0.15 μA•cm^{-2}
- Sample transfer with no additional air exposure by use of an inert gas (dry N_2) glove box
- X-ray Photoelectron Spectroscopy was used to verify surface composition after preparation steps



- **Local photoemission spectra (PES) :** Intensity (I) vs. Voltage (V)
  –Take a set of images (stack) while sequentially varying the start voltage (V_S). Extract vacuum level cutoff (E_{vac}) threshold at each pixel.

Grain-to-grain variation of the vacuum level indicates work function variation. Vacuum level and ionization energy profiles track one another.



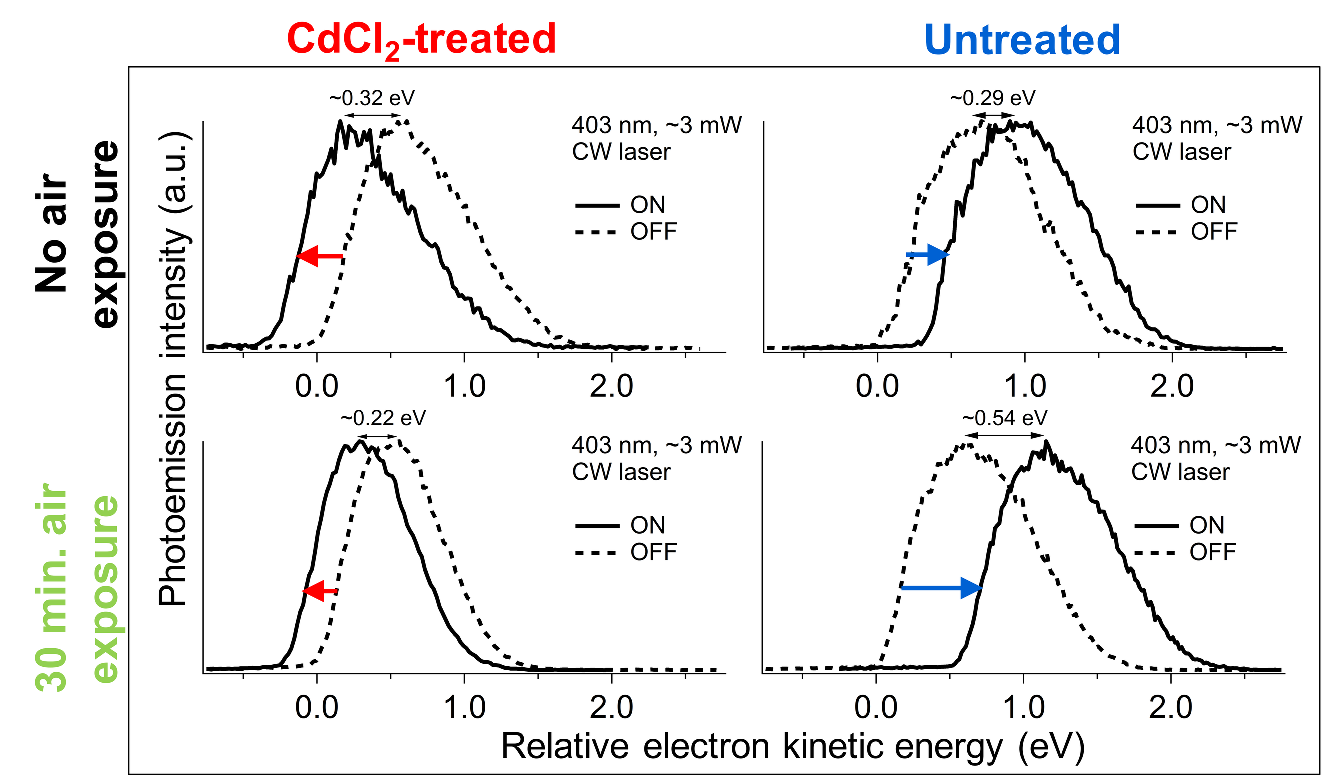
Grain-to-grain variation results in stepwise-like variation in the vacuum level and ionization energy profiles.

E_{vac} and IE profiles deviate after air exposure.

Dips in E_{vac} (red), consistent with GB downward bending suggested by scanning probe microscopy and electron-beam-induced current studies.

E_{vac} + IE decrease at GBs suggests a change in local chemical environment. Decrease in **E_{vac}** alone at GBs suggests electrostatic effects.

- **Surface photovoltage measurements (SPV):** Intensity (I) vs. Voltage (V), with and without add'l illumination
  –Note the shift in PES spectra at each pixel.



Oxygen decreased/increased E_{vac} shifts for $CdCl_2$-treated/untreated CdTe. Along with ionization energy trends, this suggests that oxygen hole dopes CdTe films.

Additional illumination shifted E_{vac} to **lower energy** for $CdCl_2$-treated CdTe ⇒ **upward** surface band bending, while E_{vac} shifted to **higher energy** for untreated CdTe, indicating **downward** surface band bending.

The general model of SPV interprets the switch from **upward** to **downward** surface band bending as inversion from **p-type** to **n-type**.

Conclusions and Impacts

We use the local information of electronic bands that PEEM provides to determine processing-structure-property-performance-relationships in CdTe. The effects of $CdCl_2$ treatment and air exposure on CdTe surfaces were investigated. In addition to identifying individual effects, we found that both $CdCl_2$ treatment and air exposure were necessary to activate grain boundaries.

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